MAY 10 1935

UNITED STATES DEPARTMENT OF COMMERCE

+

Journal of Research

of the

National Bureau of Standards

Vol. 14, No. 4 April 1935

CONTENTS

RP	TITLE AND AUTHOR	Page
775.	Accuracy of high-range current transformers. John H. Park. [Price 5c]	367
776.	Standard conditions for precise prism refractometry. Leroy W. Tilton. [Price 5c]	393
777.	Effect of granulometric composition of cement on the properties of pastes, mortars, and concretes. J. Arthur Swenson, Lacey A. Wagner, and George L. Pigman. [Price 5c]	419
778.	Chemical reactions in the lead storage battery. George W. Vinal and D. Norman Craig. [Price 5c]	449
779.	Relation of ink to the preservation of written records. Elmer W. Zimmerman, Charles G. Weber, and Arthur E. Kimberly. [Price 5c]	463
780.	Recent studies of the ionosphere. Samuel S. Kirby and Elbert B. Judson. [Price 5c]	469
781.	Infrared spectra of noble gases (10500 to 13000 A). William F. Meggers. [Price 5c]	487
782.	Effect of calcium chloride on portland cements and concretes. Paul Rapp. [Price 5c]	499
783.	Arc spectrum of copper in the infrared. C. C. Kiess. [Price 5c]	519

+

The articles listed above may be purchased (see cover page II) separately at the prices indicated in the table of contents

A monthly periodical of pure and applied science published by our National Government

Journal of Research

of the

National Bureau of Standards

¶The January 1935 issue of the Journal of Research of the National Bureau of Standards began the fourteenth semiannual volume of this periodical. The JOURNAL contains the Bureau's research papers and critical reviews in the fields of science and technology. ¶Fundamental researches always in progress in the Bureau's laboratories have their outlet in the Journal of Research of the National Bureau of Standards. If you are interested in following the new developments in science and technology, you should receive the JOURNAL. If you are already a subscriber, continue your subscription; if not, you are invited and urged to send in your subscription at once.

Technical News Bulletin

¶This is a monthly publication containing short articles reporting progress of work in the Bureau's laboratories, abstracts of papers which appear in the Journal of Research of the National Bureau of Standards, reports of scientifi and technical meetings in which the Bureau has taken part, and a list of all publications by members of the staff, and other topics within the Bureau's fields. This publication is designed primarily to give its subscribers a general review of important and timely activities and accomplishments at the Bureau. The material is presented in brief, but adequate, form for the information of those who are interested in the general activities of the Bureau. It is a prompt and reliable official source of information. If you are not already a subscriber to this monthly periodical you are urged to place your subscription.

ANNUAL SUBSCRIPTION	Prices	
	United States, Canada, Cuba, Mexico, Newfoundland, Republic of Panama	Other countries
Journal of Research of the National Bureau of Standards:		
12 monthly issues (2 volumes), paper covers	$2.50	$3.25
Bound volume (½ year, 1 volume), blue buckram . . .	3.00	3.50
Technical News Bulletin, 12 monthly issues	.50	.70

Research Papers, reprinted individual articles appearing in the Journal of Research, are available from the Superintendent of Documents shortly after appearance of monthly issue of the JOURNAL.

Address orders only to
Superintendent of Documents, U. S. Government Printing Office,
Washington, D. C.

UNITED STATES DEPARTMENT OF COMMERCE
DANIEL C. ROPER, Secretary
NATIONAL BUREAU OF STANDARDS
LYMAN J. BRIGGS, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 14, Number 4

April 1935

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1935

For sale by the Superintendent of Documents, Washington, D. C. - - - - - Price 25 cents
$2.50 per year on subscription

The prices of the separate Research Papers appearing in this Journal are given on the front cover page. A 25-percent discount is allowed when ordering 100 or more copies of any separate.

This arrangement provides a prompt and convenient method whereby readers of the Journal of Research desiring copies of separate Research Papers appearing therein may send their orders and remittances without delay to the Superintendent of Documents, United States Government Printing Office, Washington, D. C., and will aid him in determining the number of copies to be printed for sale.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP775

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

ACCURACY OF HIGH-RANGE CURRENT TRANSFORMERS

By John H. Park

ABSTRACT

The variations in ratio and phase angle of a current transformer caused by changes in the geometrical configuration of its primary circuit were determined experimentally for transformers of various makes and designs with primary current ratings from 1,200 to 7,500 amperes. A theoretical explanation of the results is given.

CONTENTS

	Page
I. Introduction	367
II. Theory	368
III. Test methods	372
IV. Results	373
1. Transformers with cores of rectangular shape and secondary windings equally distributed on all four legs	374
2. Transformers with cores of rectangular shape and secondary windings in two equal sections on opposite legs	380
3. Transformers with cores of rectangular shape and secondary windings on one leg only	382
4. Transformers with cores of ring shape and secondary windings uniformly distributed around the cores	390
V. Conclusions	392

I. INTRODUCTION

Commercial measurements of electric power and energy, in circuits carrying alternating currents of large value, are invariably made by the use of current transformers which supply, to the measuring instruments proper, secondary currents which are a replica to a reduced scale of the corresponding currents in the primary circuit. In important installations the proportionality factor or "ratio" of the transformer is obtained by an experimental comparison between the transformer in question and a standard transformer of known ratio. This comparison is usually made in the testing laboratory of the utility company concerned, while the standard transformer in turn is tested at suitable intervals by some "absolute" method usually in a large standardizing laboratory such as that of the National Bureau of Standards.

It is evident that the accuracy of the final results would be invalidated if the conditions under which either the working or the standard transformer is operated were allowed to differ to a significant extent from the conditions under which either transformer was tested. With ordinary care such conditions as frequency and secondary burden can be readily reproduced with sufficient fidelity, and the effect of changes in these conditions decreases in general with an increase in the current

to be measured, and hence in the commercial importance of the measurement.

The variations in the magnetic effect of the primary circuit resulting from changes in its geometrical configuration, however, while negligible in multi-turn transformers of low current rating, tend to increase as the rated primary current increases. The arrangement of the primary circuit in the neighborhood of the working current transformer when in service is, of course, fixed by external considerations and the question arises as to how closely this arrangement must be duplicated in the testing laboratory if significant errors are to be avoided. Similarly, the closeness with which the circuits used with the standard transformer in the testing laboratory should be duplicated in the standardizing laboratory, becomes a matter for study and perhaps for standardization by mutual agreement.

The effect on the ratio and phase angle of a current transformer of changing the arrangement of its primary circuit has been studied by Price and Duff [1] on a number of transformers of ratings up to 1,600 amperes. In view of the extension in 1932 of the facilities at the National Bureau of Standards for testing current transformers up to 12,000 amperes, it seemed desirable to extend this study into the higher range where, presumably, the effects would be enhanced. Such a study would serve to bring out the precautions needed in this range of testing to fully utilize the precision available.

II. THEORY

The relation between the primary and secondary currents of a current transformer can be deduced by considering its magnetic circuit, provided all currents and fluxes are assumed to vary sinusoidally with time and their effective values are used as vectors. For simplicity, this relation will first be derived for the hypothetical case in which the air or other medium surrounding the current transformer core is assumed to have zero permeability. Under these conditions, for any arrangement of the windings, all of the magnetic flux produced by the primary and secondary ampere-turns will make a complete circuit in the core. An example is shown in figure 1A, in which

I_1=primary current,
I_2=secondary current,
n_1=number of primary turns,
n_2=number of secondary turns, and
ϕ=total flux at any section of the core.

The equation for the sum of the magnetomotive forces around the closed magnetic circuit a b c d a is:

$$I_1 n_1 + I_2 n_2 + I_e n_1 = 0 \tag{1}$$

All of the terms in this equation are vectors and $I_e n_1$ represents the ampere-turns required to sustain the flux ϕ in the core.

The exciting ampere-turns, $I_e n_1$, may be obtained experimentally as a vector function of the voltage induced in an exploring coil wound around the core (i. e., by using either the primary or the secondary winding as an exciting coil and measuring the components of the volt-

[1] H. W. Price and C. K. Duff, *Through Type Portable Current Transformers.* Univ. Toronto, School Eng. Research Bul. 2, sec. 4, pages 202 to 210 (1921).

age induced in the exploring coil in time phase and in time quadrature with the exciting current for various values of exciting ampere-turns). Thus, if the voltage induced in the exploring coil is measured as a vector with respect to I_2 when the transformer is performing its normal function, $I_e n_1$ can also be obtained as a vector with respect to I_2 and then by use of equation 1 the vector relation between I_1 and I_2 can be computed, from which the ratio and phase angle of the transformer are readily obtainable.

For the practical case where the medium surrounding the core does not have zero permeability, the flux distribution will be about as shown in figure 1B, in which some of the flux occupies leakage paths through the air. Thus, the core flux and likewise the electromotive force induced in an exploring coil wound around the core are not constant for various sections along the perimeter of the core, and the $I_e n_1$ term in equation 1 cannot be obtained in the simple manner outlined for the hypothetical case. However, the equation for the

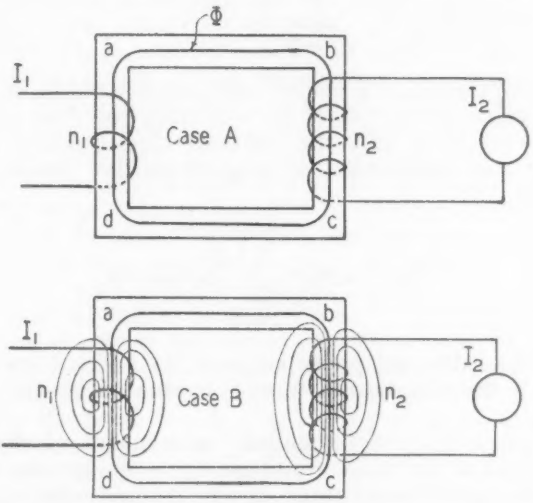


FIGURE 1

sum of the magnetomotive forces around the closed magnetic circuit a b c d a will still be the same if the value of exciting ampere-turns, $I_e n_1$, is obtained by adding vectorially, for the entire core, the ampere-turns required to maintain the flux in each elemental length of the core.

The summation of the exciting ampere-turns can be determined experimentally if the core flux is assumed to be uniform over any cross section and if all of the flux lines are considered to be perpendicular to the core cross section. In order to do this, a number of exploring coils must be wound on the core, spaced short distances apart along the core perimeter. Then, while the transformer is being used to measure a current of constant value, the electromotive force induced in each exploring coil and its phase relation with the secondary current are measured. These values are plotted against the distance along the core perimeter and by use of these curves the perimeter is divided into small lengths over which the induced electromotive

force and its phase angle with respect to the secondary current are taken to be constant. The values of exciting ampere-turns and their phase angles with respect to the secondary current, for each small length of the core, are now obtained by use of the vector relation between the exciting ampere-turn and induced electromotive force. This relation is determined as outlined in the hypothetical case, except that the exciting turns must now be uniformly distributed around the core so that the core flux will be the same at different sections. The total exciting ampere-turns and their phase angle with respect to the secondary current are obtained by adding vectorially the values of exciting ampere-turns for each small section of the core. If x is the distance along the perimeter of the core from a fixed point to any other point, and if l is the total perimeter, the exciting ampere-turns for the entire core may be expressed as:

$$\sum_{x=0}^{x=l} \frac{I_e n_1}{l} \Delta x, \tag{2}$$

where $I_e n_1$ is obtained as a vector with respect to the secondary current for any value of x by use of the exploring-coil data and the vector relation between $I_e n_1$ and the induced electromotive force. The equation for the summation of magnetomotive forces around the core becomes

$$I_1 n_1 + I_2 n_2 + \sum_{x=0}^{x=l} \frac{I_e n_1}{l} \Delta x = 0 \tag{3}$$

from which the ratio and phase angle of the current transformer can be obtained if the summation term is evaluated by the method just described.

This analysis is not recommended [2] as a means of obtaining exact numerical values of the ratio and phase angle of a current transformer, because (1) the transformer must be constructed with a large number of search coils wound on its core, (2) the task of determining the electromotive force induced in these search coils for each value of secondary current is time consuming, and (3) the assumption that the flux density is uniform over any cross section of the core is never realized and in most cases the errors thus introduced will not be negligible. This analysis is, however, useful as a qualitative guide to an understanding of how changes in location of the primary conductors affect the ratio and phase angle of a current transformer.

Since the performance of a current transformer is dependent upon the values of core flux at each cross section of the core along its perimeter, the location of the primary conductors will affect ratio and phase angle by affecting the values of core flux. However, in order to determine the qualitative effect on ratio and phase angle for a given change in arrangement of the primary circuit, further deduc-

[2] It may be useful quantitatively in the case of a current transformer with a ring-shape core and uniformly distributed windings, since the core flux will then be the same at all cross sections of the core and one exploring coil measurement will be sufficient for each value of current.

tions are required. Price and Duff [3] have demonstrated that the flux at any cross section of the core may be thought of as divided into two components. One component is called the working or mutual flux. It makes a complete circuit in the core, linking all of the primary and secondary turns, and is the same at all cross sections of the core. The other component is called the leakage flux (primary leakage flux if produced by primary turns and secondary if produced by secondary turns). It does not make a complete circuit in the core but "leaks" out and completes its circuit through the surrounding medium. This component varies at different cross sections around the core and its magnitude depends upon the arrangements of the primary and secondary turns. Price and Duff separated the total flux at any cross section of the core into these two components by an experimental method. They supplied the primary winding and the secondary winding independently so that their values of ampere-turns were exactly equal and 180° apart in phase. For these conditions, equation 3 shows that the summation of the exciting ampere-turns around the core is zero. Also, the flux at various sections of the core is substantially the same as the leakage flux during normal operation of the transformer, and since the leakage flux is usually much larger than the mutual flux, especially in high-range current transformers with nonuniform distribution of primary windings around the core, the addition of the mutual flux will not greatly affect the magnetic condition of the core and the summation of the exciting ampere-turns required to produce the leakage flux in the core will still be zero. Therefore, the leakage flux will have no direct effect upon the summation term in equation 3. However, there will be an indirect effect, because the existence of the leakage flux will increase the flux density in the core and change its magnetic condition, thus changing the ampere-turns required to produce the mutual flux and, correspondingly, the ratio and phase angle of the current transformer. If the addition of leakage flux to mutual flux does not bring the total flux density at any cross section of the core above the value for maximum permeability, the number of ampere-turns required to produce the mutual flux will be decreased by the presence of the leakage flux. If the addition of leakage flux to mutual flux does bring the total flux density at any cross section of the core materially above the value for maximum permeability, the number of ampere-turns required to produce the mutual flux may be much increased. Thus, according to its magnitude, the addition of leakage flux may either increase or decrease the ratio and phase angle.

Leakage flux will also affect ratio and phase angle by causing a leakage reactance in the secondary winding. This leakage reactance may be defined as the integrated value per unit current of the linkages of secondary leakage flux with secondary turns minus the linkages of primary leakage flux with secondary turns. The contribution of secondary leakage flux is usually the larger, thus introducing a positive secondary leakage reactance, which has the same effect on ratio and phase angle as the addition of inductive burden, i. e., it decreases the phase angle and increases the ratio. However, for certain arrangements of primary circuit the contribution from the primary leakage flux will be the larger, thus making the secondary

[3] *Effects of magnetic leakage in current transformers*, Univ. Toronto, Bul. 2, sect. 4, pages 167 to 191 (1921).

leakage reactance in effect negative. This will tend to make the phase angle larger and the ratio smaller. If the effective negative secondary leakage reactance is more than enough to balance the inductive reactance in the burden, it will make the secondary induced voltage (see fig. 2) lag the secondary current and the mutual flux lead the secondary current by less than 90 degrees. In extreme cases the exciting ampere-turns required to produce the mutual flux may also lead the secondary current by less than 90 degrees, thus making the ratio of primary ampere-turns to secondary ampere-turns less than one.

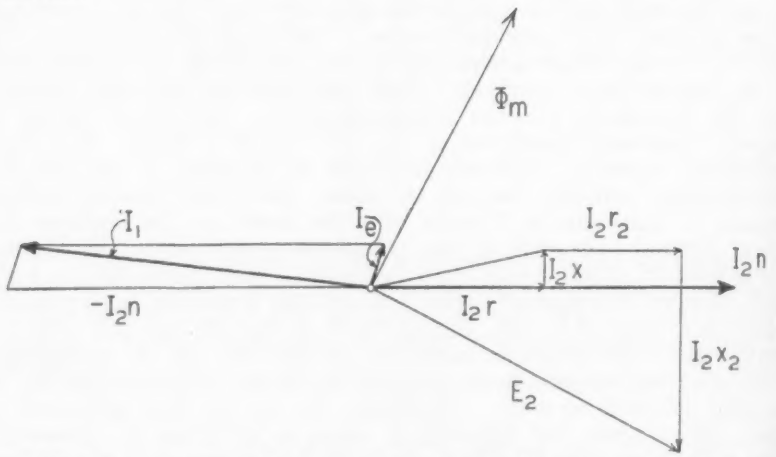


FIGURE 2.—*Vector diagram for a current transformer whose arrangement of primary turns is such that the secondary leakage reactance is negative in effect.*

I_1=primary current
I_2=secondary current
I_e=exciting current
E_2=secondary induced voltage
n=turn ratio
r=resistance of burden
x=reactance of burden
r_2=resistance of secondary winding
x_2=secondary leakage reactance
ϕ_m=mutual flux

A change in arrangement of primary circuit affects the performance of a current transformer by changing the leakage fluxes in and near the core. A change in the frequency of the current being measured or in the burden of the secondary circuit will not greatly affect the leakage flux. Therefore, for a given change in arrangement of primary circuit, the change in performance will be practically independent of the frequency and secondary burden, although the actual performance of the current transformer may change appreciably for different frequencies or secondary burdens.

III. TEST METHODS

In the present study, the ratio and phase angle of current transformers of each of the several main classes of design used in practice for measuring currents of 2,000 amperes or more, were determined with various arrangements of primary circuit. The equipment and methods regularly employed in testing transformers at the National Bureau of Standards [4] were used. The primary current circuit of this equipment, as shown by figure 3, consists of large copper slabs which connect the supply transformer, the transformer under test, and

[4] *Equipment for testing current transformers*, BS J.Research **11**, 93 (1933) RP580.

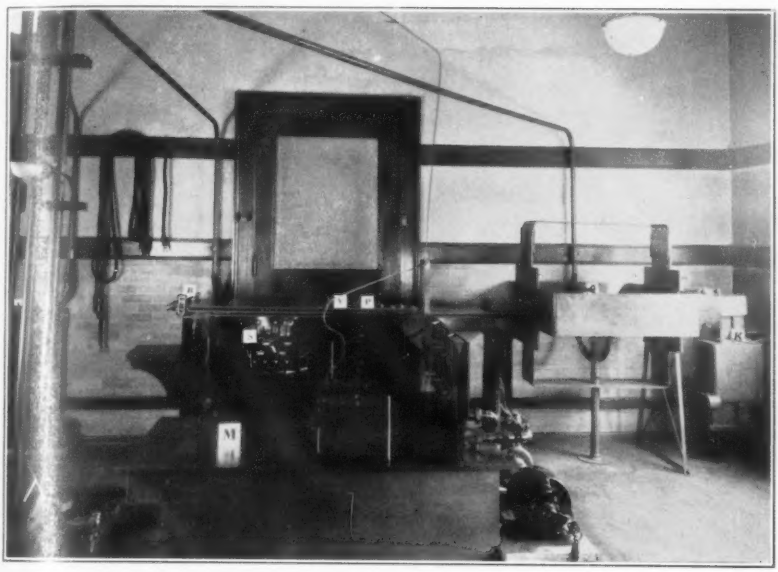


FIGURE 3.—*Primary circuit of equipment for testing current transformers, arranged as ordinarily used at the National Bureau of Standards.*

S, Standard current transformer; O, transformer under test; K, supply transformer; M, tank containing oil-cooled primary shunts.

the standard transformer or primary shunt in series. This circuit is so arranged that two copper slabs carrying current in opposite directions are face to face and close together throughout the entire circuit except where the transformer under test is connected. Here, a portion of the copper slab (called the inner conductor) carrying current in one direction is replaced by the primary of the transformer under test if it is of the busbar type; if it is of the hole type the copper slab is used as the conductor through its core window. The copper slab (called the return lead) carrying current in the opposite direction is close to the inner conductor up to two points 18 inches from the center of the transformer being tested. At each of these points the return lead is connected to a copper plate whose flat surface is perpendicular to the inner conductor. The circuit is completed by four copper slabs connecting these plates together. For the regular testing at the National Bureau of Standards, the arrangement of these slabs is as shown in figure 3. For the present study various numbers and location of these slabs were used. In order to arrange the primary circuit as a loop or loops around one or more sections of the core, flexible cables were used to construct the desired shape of primary circuit and these cables were then clamped to the heavy copper slabs at such a point that stray fields from the rest of the primary circuit would not affect the performance of the transformer. By using one or the other of these procedures for connecting the primary of the transformer under test, it was possible to obtain nearly any desired arrangement of primary circuit.

Exploring coils were wound on the cores of some of the experimental transformers and the electromotive forces induced in these coils, while the transformers were being tested at currents near their rated values, were measured by a separately excited voltmeter. From these measurements the core flux density at the location of each exploring coil was computed and the results show whether that section of the core was operating above or below the value of flux density for maximum permeability.

IV. RESULTS

Nearly all current transformers with a primary rating of 2,000 amperes or more have primary windings consisting of a single conductor passing through the opening of a single-window core and according to their design may be divided into the following groups: (1) transformers with cores of rectangular shape and secondary turns equally distributed on all four legs, (2) transformers with cores of rectangular shape and secondary turns in two equal sections on opposite legs, (3) transformers with cores of rectangular shape and secondary turns all on one leg, and (4) transformers with cores of ring shape and secondary turns uniformly distributed around the core. For all transformers of any one group, a given change in arrangement of primary circuit produces similar changes in ratio and phase angle, but the actual value of these changes depends upon the size and magnetic properties of the core and the rated primary ampere-turns. No attempt was made to obtain sufficient data so that the quantitative effect of changing the location of the primary conductors could be deduced for all transformers of various nominal currents and with cores of various sizes and magnetic properties. However, data were obtained on at least one current transformer of each of the above

groups. These data are intended to show only the arrangements of primary conductor which are most likely to give the best performance for any transformer of each group, and approximately the order of magnitude of the changes caused by departures from these arrangements.

1. TRANSFORMERS WITH CORES OF RECTANGULAR SHAPE AND SECONDARY WINDINGS EQUALLY DISTRIBUTED ON ALL FOUR LEGS

Current transformer A_1, a description of which is given in table 1, was tested with various arrangements of a single primary turn. The turn ratio, 1499:1, was used as the nominal ratio in the computations. The curves in figures 4 to 7 show the ratio correction factor (the quantity which multiplied by nominal ratio gives true ratio) and the phase angle (the angle by which the reversed secondary current leads the primary current) plotted against secondary current for various arrangements of primary circuit. Because of limitations in the source of power supply, it was not possible to test this transformer at the 5-ampere value of secondary current in all instances, but a test point was taken as near the 5-ampere point as possible and it was at least 4 amperes in all cases.

Curves 1 in figure 4 show the performance of transformer A_1 with a straight conductor through the center of the core window and the return lead in four sections, equally spaced around the inner conductor, parallel to it, and 20 inches from it. This arrangement of primary circuit is the one ordinarily used at the National Bureau of Standards in testing current transformers for 1,000 amperes or over; also, it is in effect equivalent to a single return lead at a great distance from the inner conductor. It will be called the normal arrangement in the present discussion, and on each figure, curves 1 represent the performance of the transformer with this normal arrangement of primary circuit. Curves 1 will thus serve as a basis of reference for judging the magnitude of the errors when other arrangements of primary circuit are used.

With the normal arrangement of primary circuit, very little of the primary leakage flux passes through the core or links any secondary turns, and as seen by curves 1 of figure 4, the performance of transformer A_1 is quite normal under these conditions. Curves 2 show the performance with the primary consisting of a loop (12 inches in diameter) of large cable around leg "a" of the core. Under these conditions a large amount of primary leakage flux passes through part of the core and links some of the secondary turns. At low currents this flux is not sufficient to bring the core flux density up to the value for maximum permeability, but it introduces a negative leakage reactance in the secondary winding, the effect of which was explained in the discussion of theory. In this case the negative secondary leakage reactance is sufficient to make the ratio of primary ampere-turns to secondary ampere-turns less than 1 from 0.5 to 1 ampere secondary current. For larger currents, measurements with the exploring coils showed that the leakage flux was sufficient to bring the core flux density above the value for maximum permeability. Thus, the exciting ampere-turns and hence the ratio and phase angle increase rapidly when the secondary current is raised above 3 amperes.

Curves 2 of figure 4 indicate that the performance for this arrangement of primary circuit differs from the performance with the normal arrangement by as much as 6 percent in ratio and 20 minutes in phase angle. These are probably the largest differences that can be obtained by changing the primary circuit of this transformer and they

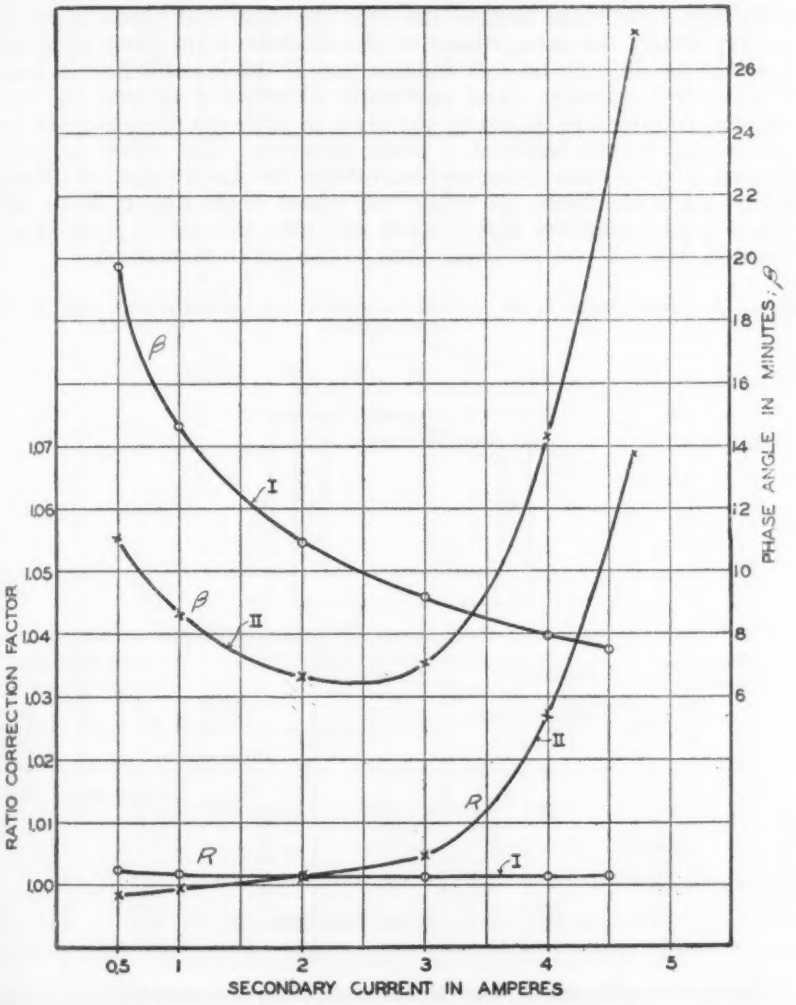


FIGURE 4.—*Performance curves for transformer* A_1

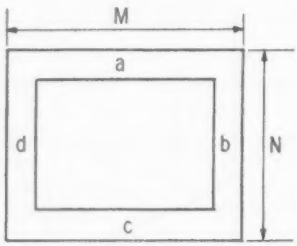
Nominal ratio $\frac{7495}{5}$. Burden 1.2 ohm and 2,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary circuit
1	Straight conductor through center of core window, one return lead opposite each leg of the core and 20 inches from center of the inner conductor.
2	A loop, 12 inches in diameter, of 2 large cables in parallel around leg "a".

will rarely occur in practice, because a current transformer such as A_1 would usually have a primary circuit consisting of a straight conductor through the center of its core window and one or more return leads parallel to the straight conductor and at various distances from

it. The curves in figure 5 show the ratio correction factor and the phase angle for a number of possible arrangements of return lead. Curves 1 show the performance with the normal arrangement, which is the equivalent of a return lead at a great distance. Curves 2 are for data obtained with the four return slabs close to the transformer. A comparison of curves 1 and 2 shows that if the return leads are uniformly distributed around the core the ratio and phase angle will be very nearly the same whatever the distance from inner conductor to return leads may be. It follows that if the transformer is tested with several primary turns uniformly distributed around the core, the performance will be nearly the same as with one central inner conductor and return leads at a great distance. The other curves in figure 5 indicate that the more nonuniform the distribution of primary return leads the more the ratio and phase angle depart from their values with a uniform distribution and that this effect is more pronounced with the return leads close to the inner conductor.

TABLE 1.—*Description of the rectangular-core current transformers used in this investigation*



Transformer		Number of secondary turns	Nominal ratio	Secondary coils on legs	Core material	Core dimensions		
No.	Type					M	N	Cross-section area
						Inches	*Inches*	sq in.
A_1	Hole	1499	7495:5	a, b, c, and d	Silicon-steel	11.5	10	1
A_2	do	729	3645:5	a and c	do	11.5	10	1
B_2	Busbar		3500:5	do	do	7	6	2.25
C_2	Hole		5000:5	do	do			
D_2	Busbar		5000:5	do	do	7.87	6	1.75
E_2	Hole		2500:5	do	do			
A_3	do	364	1820:5	a	do	11.5	10	1
F_3	Busbar		1200:5	do	Hypernik	5.75	4	1.20

The curves of figure 6 show the change in ratio correction factor and phase angle when the inner conductor is displaced from the center of the core window. With the return leads uniformly distributed around the core, the inner conductor may be considerably off center without seriously affecting the performance. When the return leads are concentrated near one leg of the core, a displacement of the inner conductor from the center causes a considerable change in ratio for secondary currents over 3 amperes. Curves 1, 2, and 4 of figure 7 show the ratio correction factor and phase angle of transformer A_1 under the same test conditions as were used in curves 1, 2, and 4 of figure 6, except that a frequency of 60 cycles per second was used in

place of 25. A comparison of these two groups of curves shows that the effect on performance of changing the position of the primary conductors is about the same at both frequencies. Curves 3 and 5

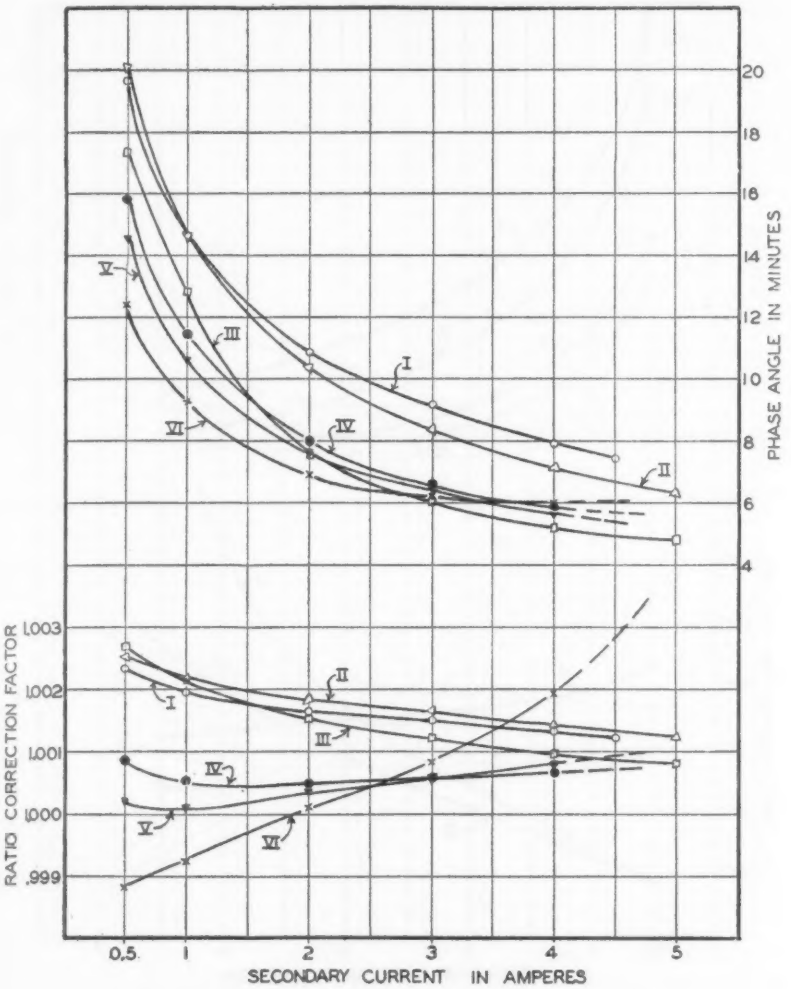


FIGURE 5.—*Performance curves for transformer* A_1

Nominal ratio $\frac{7495}{5}$ Burden 1.2 ohm and 2,000 microhenries. Frequency 25 cycles per second. Inner primary conductor in the center of the core window.

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from inner conductor.
2	One opposite each leg of the core and 8 inches from inner conductor.
3	One opposite each of legs "a" and "c" and 8 inches from inner conductor.
4	One opposite leg "a" and 26½ inches from inner conductor.
5	One opposite leg "a" and 15 inches from inner conductor.
6	One opposite leg "a" and 8 inches from inner conductor.

of figure 7 are for the same test conditions as curves 1 and 4, except that the secondary burden was much less. These curves show that the ratio and phase angle are slightly different for different burdens

but that the change in performance for the same change in arrangement of primary conductors is the same at both burdens. These results check the predictions which were made in the theory.

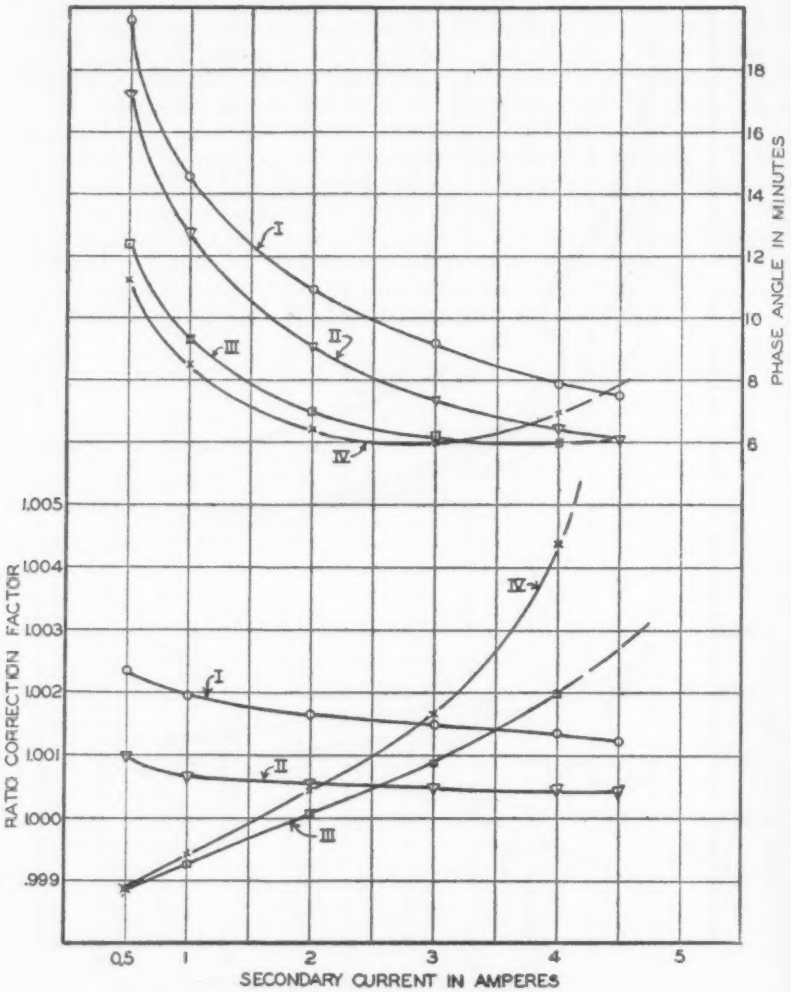


FIGURE 6.—*Performance curves for transformer* A_1

Nominal ratio $\frac{7495}{5}$. Burden 1.2 ohm and 2,000 microhenries. Frequency 25 cycles per second.

Curve	Location of inner primary conductor	Arrangement of primary return leads
1	Center of core window	One opposite each leg of the core and 20 inches from inner conductor.
2	Near leg "a"	Do.
3	Center of core window	One opposite leg "a" and 8 inches from inner conductor.
4	Near leg "a"	Do.

Since it is the change in performance of a current transformer for a change in arrangement of primary circuit which is of particular interest in this investigation, the results which follow are given for only

one frequency and burden. The change in performance for a given change in arrangement of primary circuit would be nearly the same for any ordinary burden or usual power frequency.

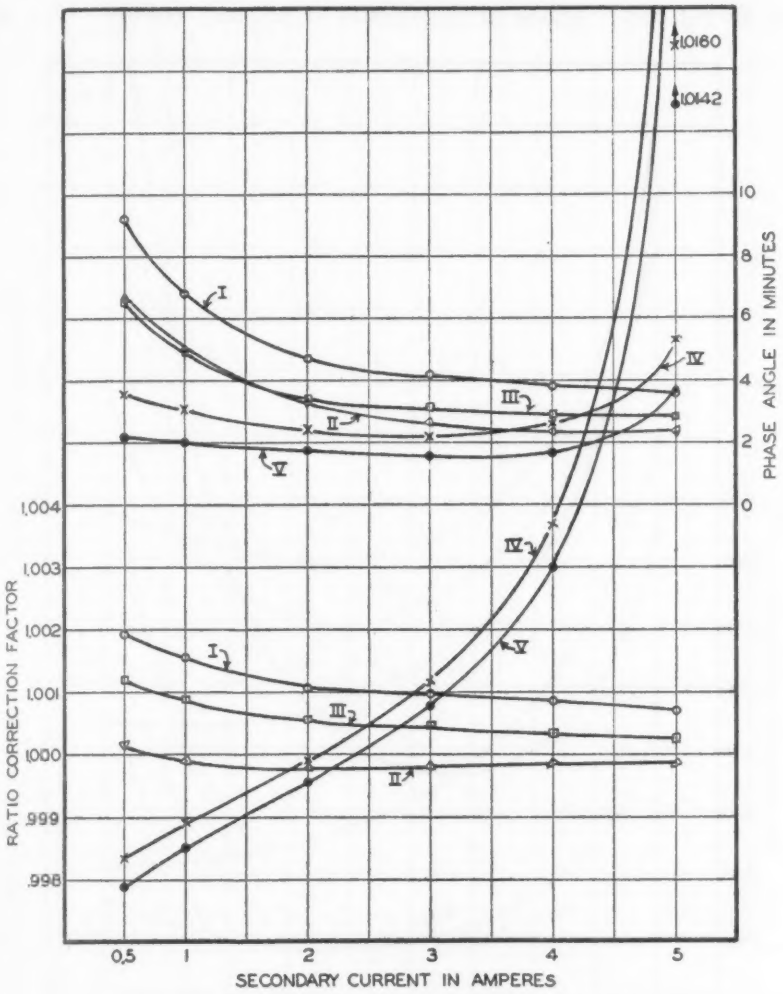


FIGURE 7.—*Performance curves for transformer* A_1

Nominal ratio $\frac{7495}{5}$. Frequency 60 cycles per second. "Burden C, 1.2 ohm and 2,000 microhenries." "Burden D, 0.26 ohm and 100 microhenries".

Curve	Burden	Location of inner primary conductor	Arrangement of primary return leads
1	C	Center of core window	One opposite each leg of the core and 20 inches from inner conductor.
2	C	Near leg "a"	Same as for 1.
3	D	Center of core window	Same as for 1.
4	C	Near leg "a"	One opposite leg "a" and 8 inches from inner conductor.
5	D	Near leg "a"	Same as for 4.

2. TRANSFORMERS WITH CORES OF RECTANGULAR SHAPE AND SECONDARY WINDINGS IN TWO EQUAL SECTIONS ON OPPOSITE LEGS

Current transformer A_2, a description of which is given in table 1, was tested with various arrangements of primary circuit. The re-

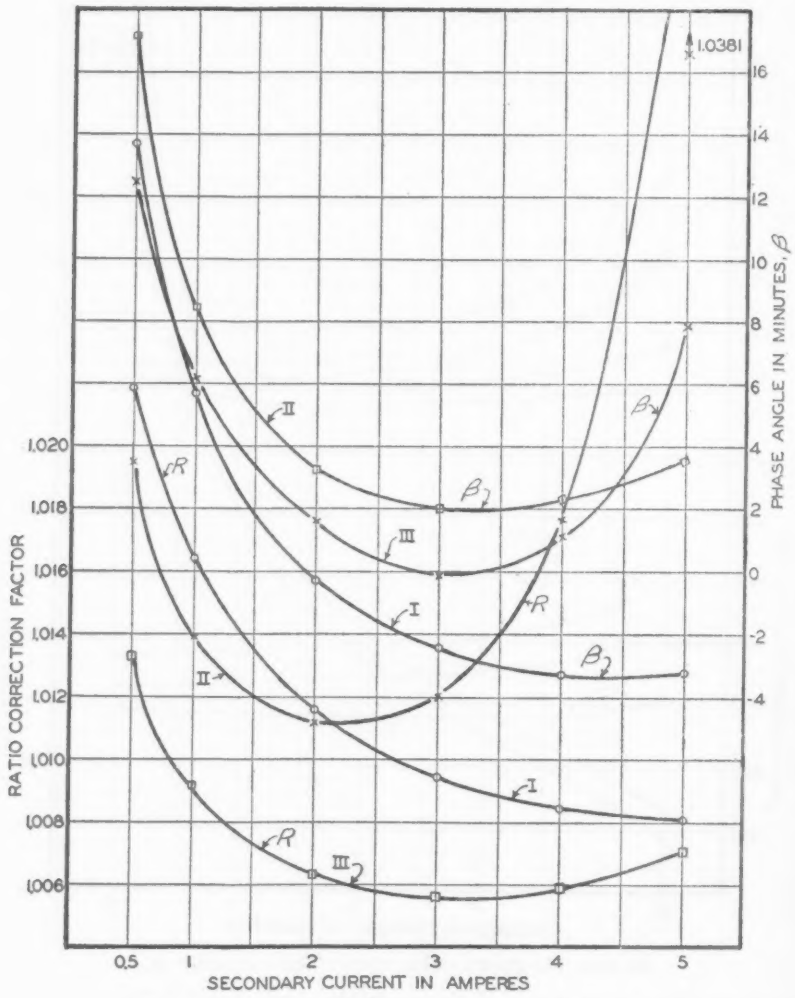


FIGURE 8.—*Performance curves for transformer* A_2

Nominal ratio $\frac{3645}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary circuit
1	Straight conductor through center of core window, one return lead opposite each leg of the core and 20 inches from inner conductor.
2	A loop, 12 inches in diameter, of large cable around leg "a".
3	A loop, 12 inches in diameter, of large cable around leg "d".

sults of these tests are shown in figures 8 to 11. The curves in figure 8 show the performance with the normal arrangement of primary circuit and with the two arrangements causing the largest difference

in ratio (a maximum of over 3 percent). These conditions are not apt to occur in practice and the results show the necessity of avoiding them.

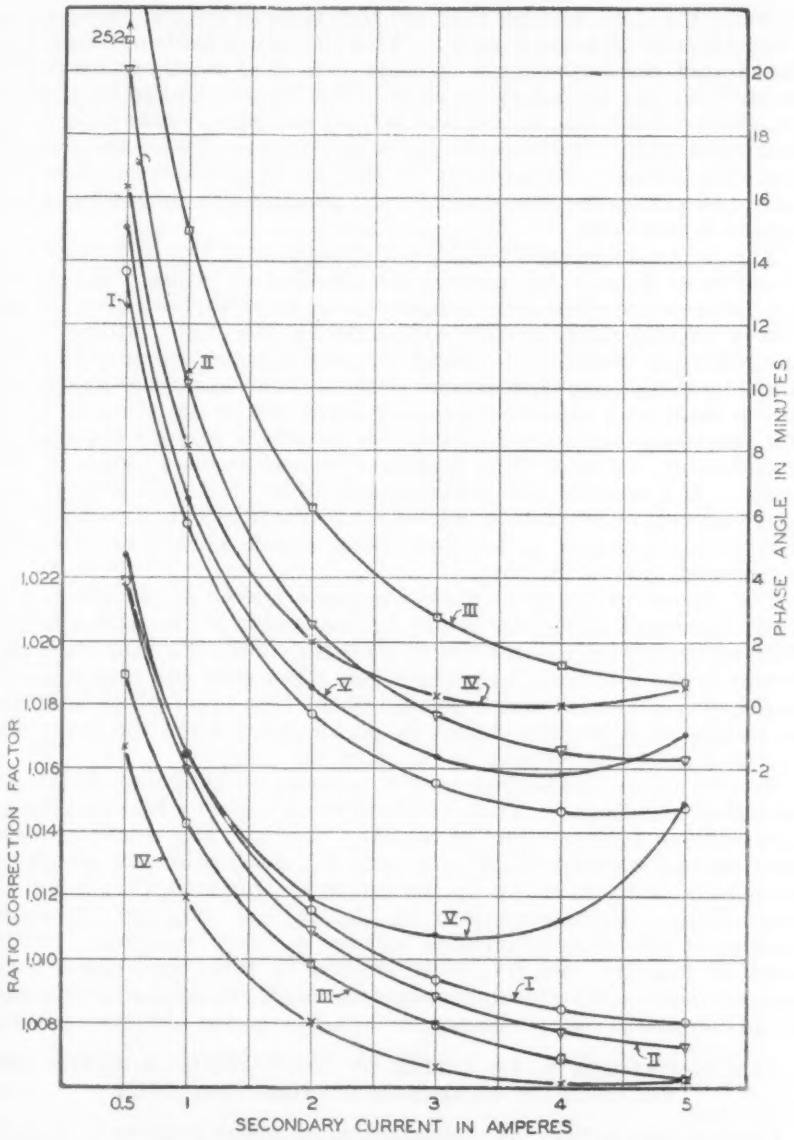


FIGURE 9.—*Performance curves for transformer* A_2

Nominal ratio $\frac{3645}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second. Inner primary conductor in the center of the core window

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from inner conductor.
2	One opposite each leg of the core and 8 inches from inner conductor.
3	One opposite each of legs "a" and "c" and 8 inches from inner conductor.
4	One opposite leg "a" and 8 inches from inner conductor.
5	One opposite leg "d" and 8 inches from inner conductor.

The curves in figure 9 show the performance with the primary consisting of a straight conductor through the center of the core window and return leads in various arrangements. With the return leads uniformly distributed around the central inner conductor the performance is nearly the same whether they are very close to the transformer or at a considerable distance from it. With the return leads not uniformly distributed, the performance depends upon their location with respect to the core and secondary winding. The largest change in performance occurs when one return lead is used and placed near a leg of the core upon which there are no secondary turns. Under these conditions the primary leakage flux in this leg of the core becomes very large and causes the flux density in it to approach saturation as the current is increased.

The curves in figure 10 show a comparison of the performance of transformer A_2 with the normal arrangement of primary circuit and the performance when eight primary turns are used, each being looped closely around the secondary coils. When the eight primary turns are uniformly distributed around the core, the performance is nearly the same as with one central inner conductor and uniformly distributed return leads; but when four primary turns are wound around each of the two secondary coils a and c, the secondary leakage reactance is considerably reduced, thus making the performance decidedly different. If a transformer of this type is to be used with one primary turn and return leads at a considerable distance but is to be tested with several primary turns, these turns should always be uniformly distributed around the core.

The curves in figure 11 show the performance of transformer A_2 when the inner conductor is not in the center of the core window. With uniformly distributed return leads the centering of the inner conductor is not extremely important, but when only one return lead is used and it is located near a section of the core upon which there are no secondary turns, the change in performance when the inner conductor is not centered may be considerable.

Several other transformers with cores of rectangular shape and secondary windings in two equal sections on opposite legs were tested with various arrangements of primary circuit. The results of these tests on transformers B_2, C_2, D_2, and E_2, descriptions of which are given in table 1, are shown by the curves in figures 12, 13, 14, and 15, respectively. Intercomparison of the results obtained on transformers of this design indicates that for a given change in arrangement of primary circuit the differences in ratio and phase angle become larger with (1) an increase in rated primary ampere-turns, (2) an increase in core perimeter, or (3) a decrease in core cross section.

3. TRANSFORMERS WITH CORES OF RECTANGULAR SHAPE AND SECONDARY WINDINGS ON ONE LEG ONLY

Current transformer A_3, a description of which is given in table 1, was tested with various arrangements of primary circuit. The curves in figure 16 show the results of the tests with the inner conductor at different locations in the window of the core and the return lead in four sections equally spaced around the inner conductor and 20 inches from it. Under these conditions the largest changes in performance are 8 percent in ratio (at 5 amperes secondary current) and 28 minutes in phase angle (at 0.5 ampere secondary current). For nonuniform distributions of return lead the changes are much greater.

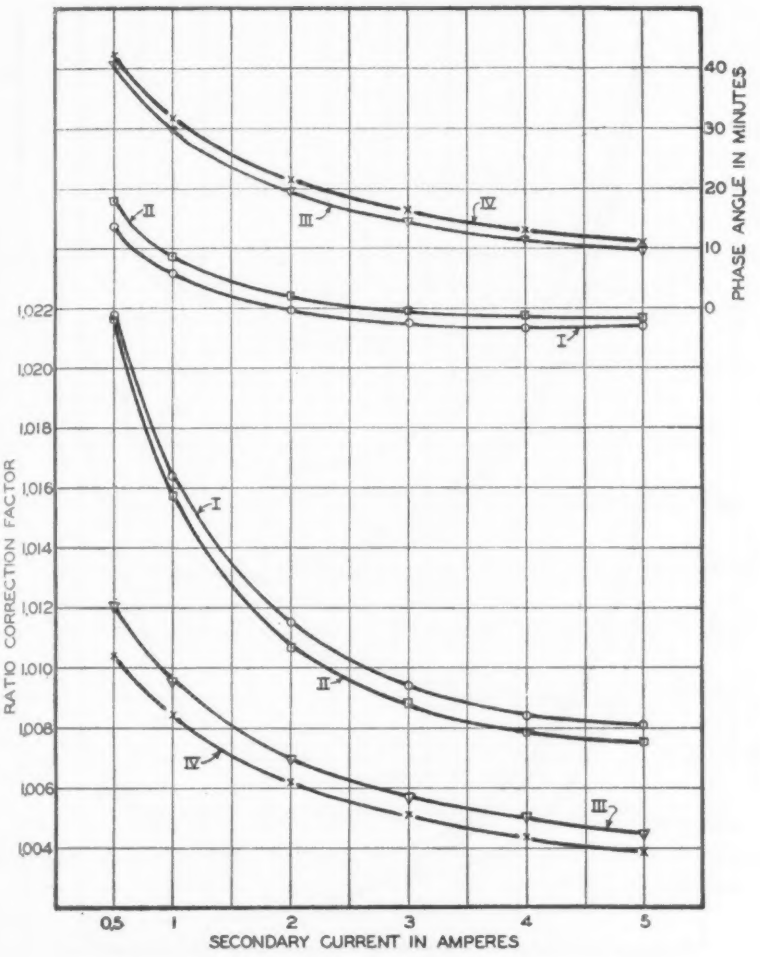


FIGURE 10.—*Performance curves for transformer* A_2.

Nominal ratio $\frac{3645}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary circuit
1	Straight conductor through center of core window, one return lead opposite each leg of the core and 20 inches from inner conductor.
2	Eight turns in series looped closely around the core, two on each leg.
3	Eight turns in series looped closely around the core, four around each of legs "a" and "c".
4	Eight turns in series looped closely around legs "a" and "c" in figures of eight.

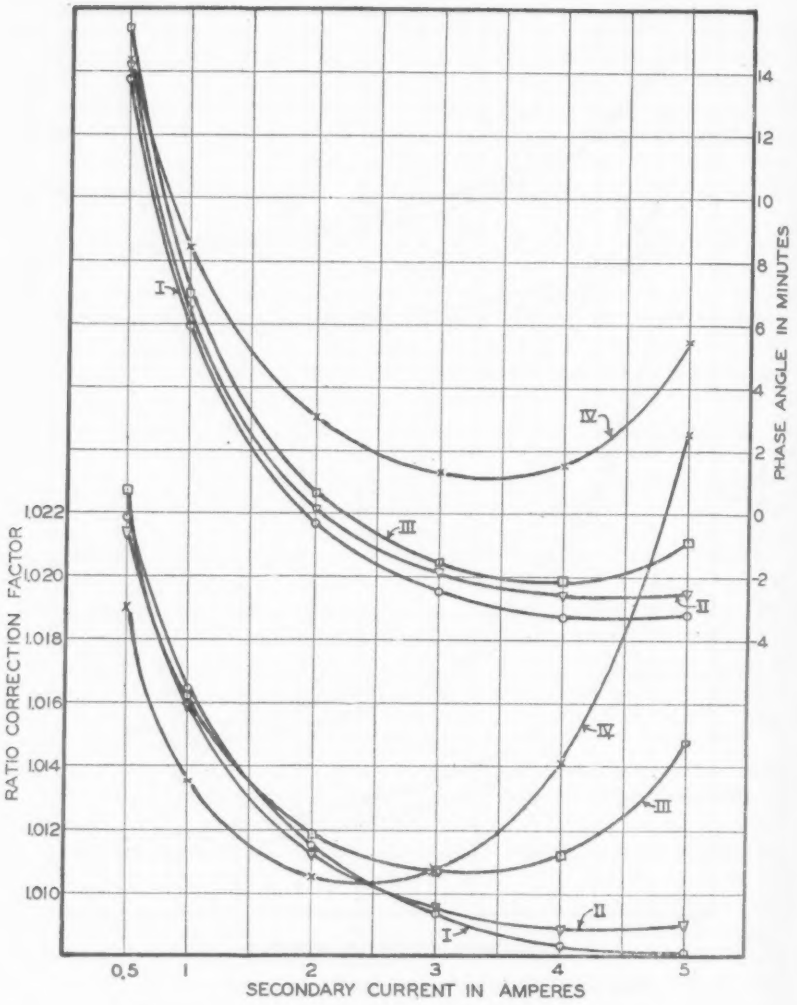


FIGURE 11.—*Performance curves for transformer* A_2.

Nominal ratio $\frac{3645}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Location of inner primary conductor	Arrangement of primary return leads
1	Center of core window	One opposite each leg of the core and 20 inches from inner conductor.
2	Near leg "d"	Same as 1.
3	Center of window	One opposite leg "d" and 8 inches from inner conductor.
4	Near leg "d"	Same as 3.

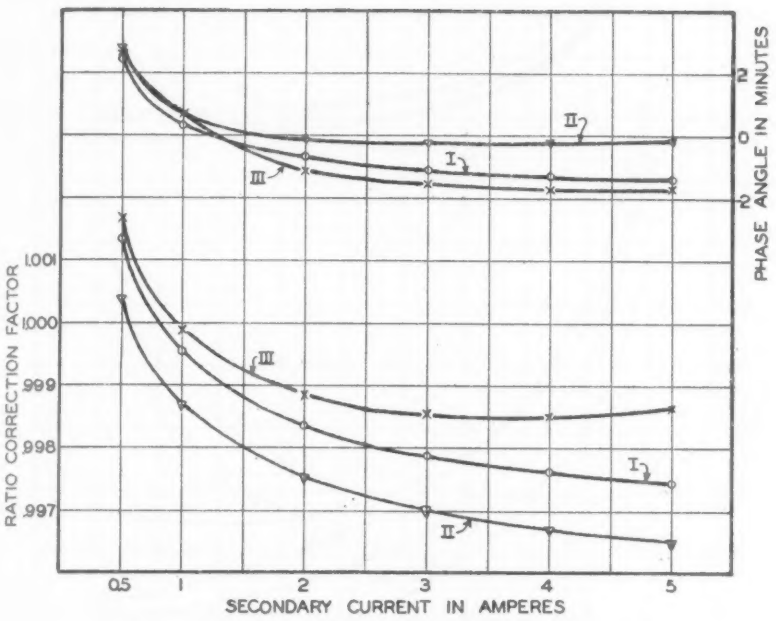


FIGURE 12.—*Performance curves for transformer* B_2.

Busbar type. Nominal ratio $\frac{3500}{5}$. Burden 0.45 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from central busbar.
2	One opposite leg "a" and 7 inches from central busbar.
3	One opposite leg "b" and 7 inches from central busbar.

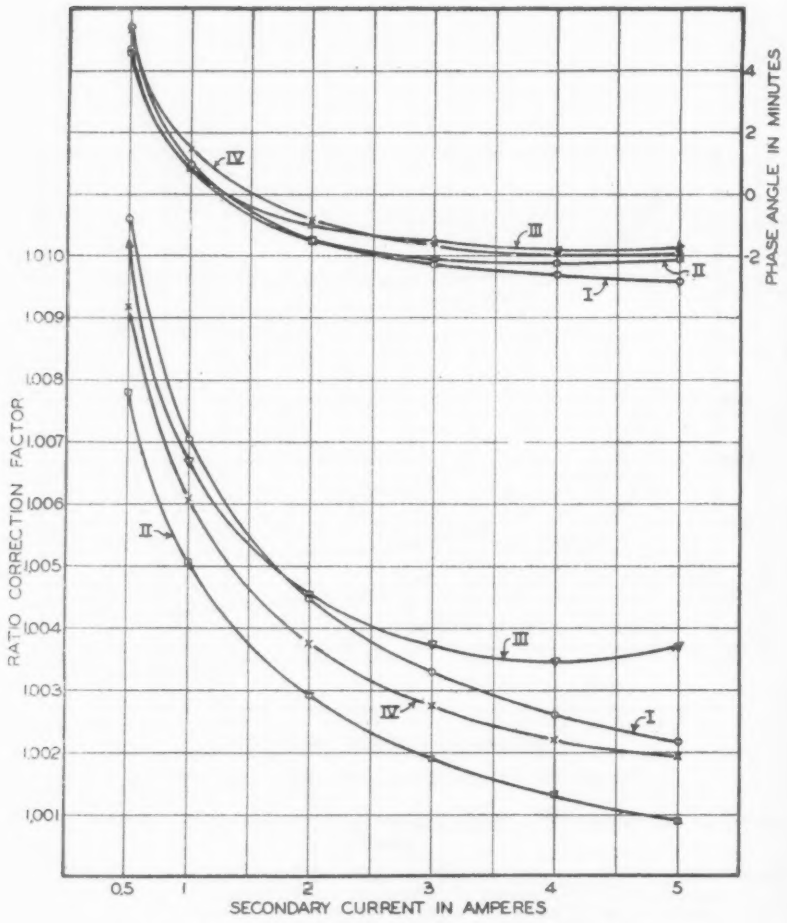


FIGURE 13.—*Performance curves for transformer* C_3.

Hole type. Nominal ratio $\frac{5000}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second. Inner primary conductor in center of core window.

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from inner conductor.
2	One opposite leg "a" and 7 inches from inner conductor.
3	One opposite leg "b" and 6 inches from inner conductor.
4	One opposite corner of legs "a" and "b" and 8 inches from inner conductor.

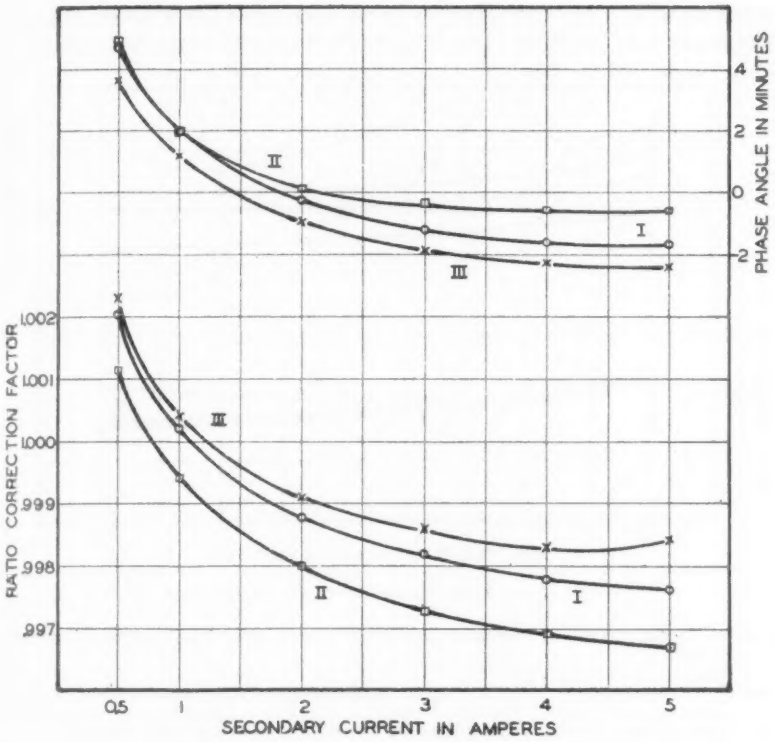


FIGURE 14.—*Performance curves for transformer* D_2.

Busbar type. Nominal ratio $\frac{5000}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from central busbar.
2	One opposite leg "a" and 5 inches from central busbar.
3	One opposite leg "b" and 5 inches from central busbar.

This transformer was constructed with a secondary coil on each leg, but only one secondary coil was used in this test. Thus, the perimeter of the core and consequently the change in performance for a given change in arrangement of primary circuit were much greater than they would be for a transformer with the same rated ampere-turns, designed with a secondary coil on one leg only. However, the ampere-turn rating of this transformer as tested was only, 1,820, and for larger current ratings the core perimeter of a transformer designed with only one secondary coil might approach that of the transformer tested. Also the changes in performance for a given change in arrangement of primary circuit increase with the ampere-turns; there-

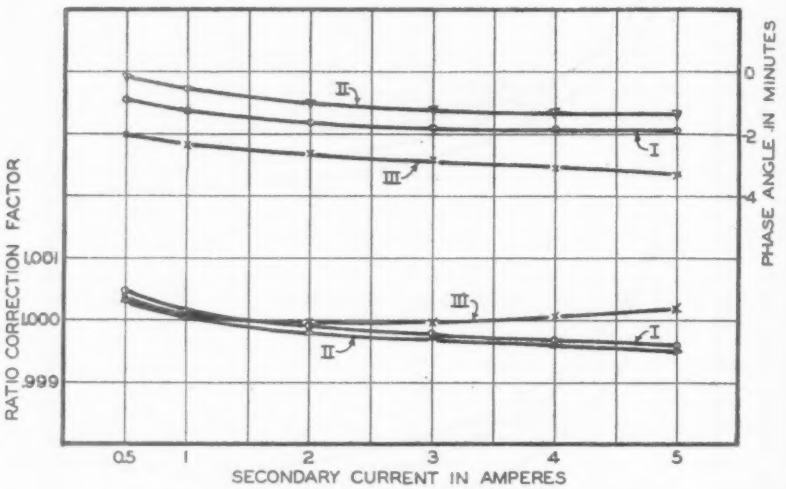


FIGURE 15.—*Performance curves for transformer* E_2.

Hole type. Nominal ratio $\frac{2500}{5}$. Burden 0.6 ohm and 1,000 microhenries. Frequency 60 cylces per second.

Curve	Location of inner primary conductor	Arrangement of primary return leads
1	Center of core window	One opposite each leg of the core and 20 inches from inner conductor.
2	Center of core window	One opposite leg "a" and 5½ inches from inner conductor.
3	Near leg "b"	One opposite leg "b" and 3½inches from inner conductor.

fore, the results for this transformer may be considered to give a fair indication of the errors for transformers of this type when they are used for large primary currents, say 3,000 amperes or over.

Current transformer F_3, a description of which is given in table 1, was tested with several arrangements of primary circuit. The curves in figure 17 show the performance of this transformer with the locations of return lead causing the largest changes in ratio and phase angle. These changes are quite small, and it may be concluded that transformers of this type are satisfactory for primary currents below 2,000 amperes if their cores are small in perimeter and large in cross-sectional area.

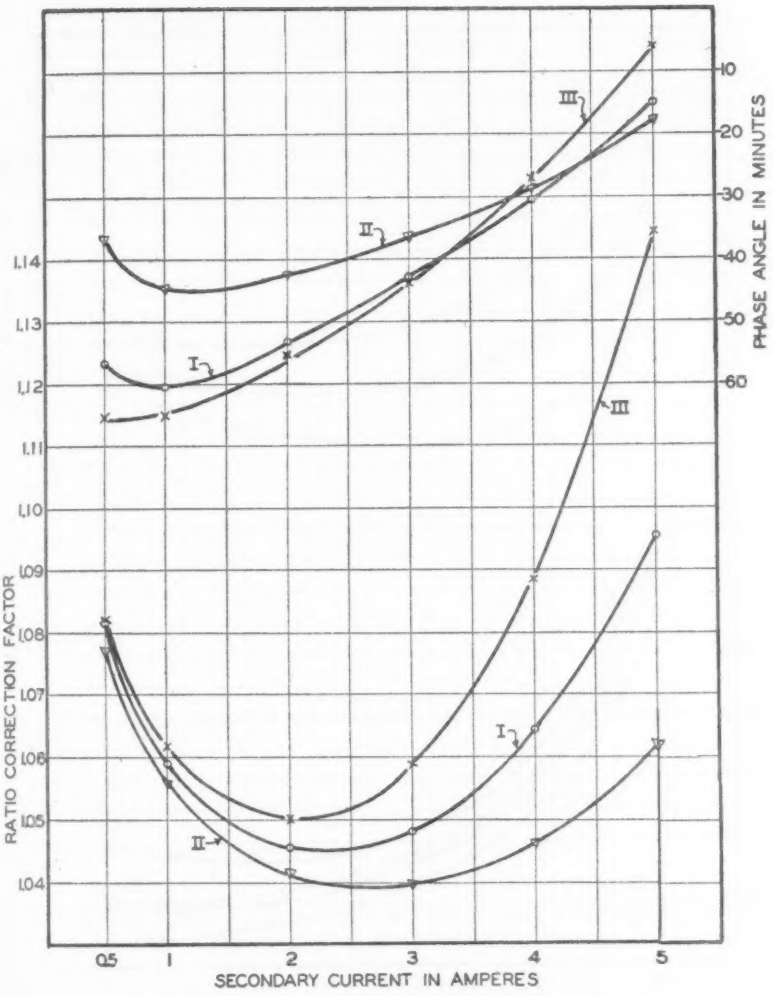


FIGURE 16.—*Performance curves for transformer* A_3.

Hole type. Nominal ratio $\frac{1820}{5}$. Burden 0.3 ohm and 500 microhenries. Frequency 25 cycles per second. Primary return lead in four sections, one opposite each leg of the core and 20 inch s from the center of the inner conductor.

Curve	Location of inner primary conductor
1	Center of core window.
2	Near leg "a".
3	Near leg "c".

4. TRANSFORMERS WITH CORES OF RING SHAPE AND SECONDARY WINDINGS UNIFORMLY DISTRIBUTED AROUND THE CORE

A 3,000-ampere hole-type current transformer with a ring-shaped core and secondary winding uniformly distributed around the core

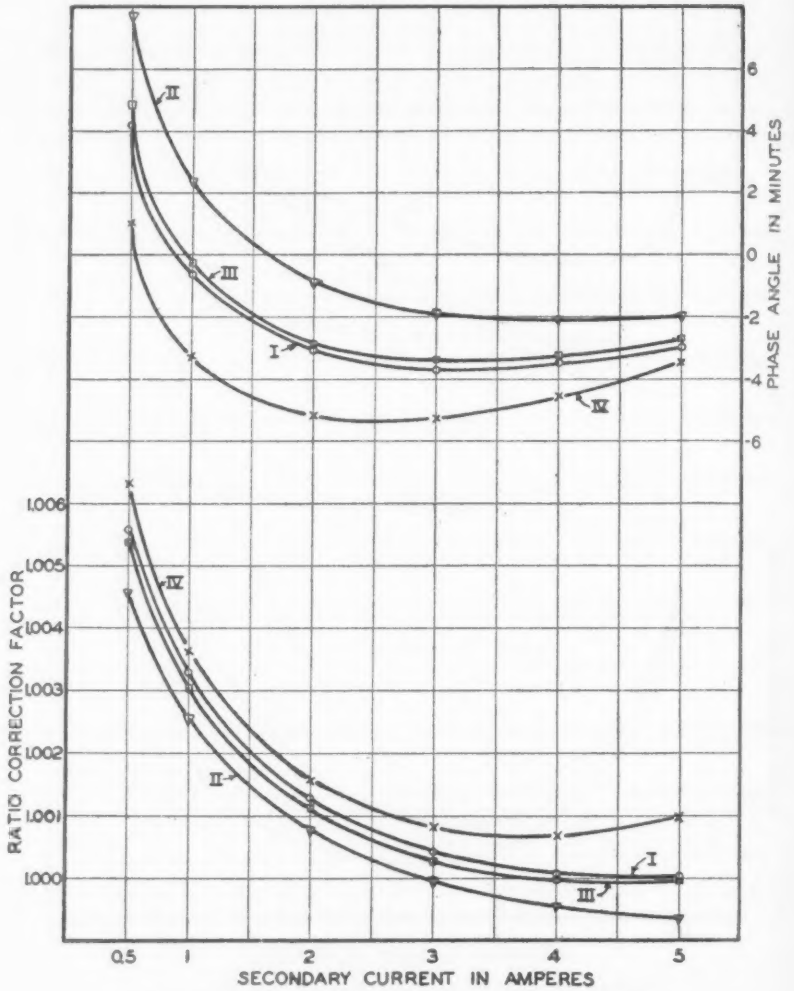


FIGURE 17.—*Performance curves for transformer* F_3.

Busbar type. Nominal ratio $\frac{1200}{5}$. Burden 0.3 ohm and 500 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary return leads
1	One opposite each leg of the core and 20 inches from central busbar.
2	One opposite leg "a" and 6 inches from central busbar.
3	One opposite leg "b" and 6 inches from central busbar.
4	One opposite leg "c" and 6 inches from central busbar.

was tested with its primary winding (1) uniformly distributed around the core and (2) concentrated on one section of the core. The differences in performance with these two arrangements of primary circuit were found to be less than 0.01 of 1 percent in ratio and 1

minute in phase angle. Therefore, the performance of this transformer was considered to be independent of the arrangement of the primary circuit. The core was made of a nickel-iron alloy and the diameter of the central opening was only 3 inches.

A 5,000-ampere hole-type current transformer, G_4, with a ring-shaped core and secondary winding uniformly distributed around the core was tested with several arrangements of primary circuit. The curves in figure 18 show the performance for the two arrangements of primary circuit giving the largest differences in ratio and phase angle. For most purposes these differences (0.07 of 1 percent or less in ratio and 4 minutes or less in phase angle) would be negligible. The core of this transformer was made of silicon steel and the central opening was about 6 inches in diameter.

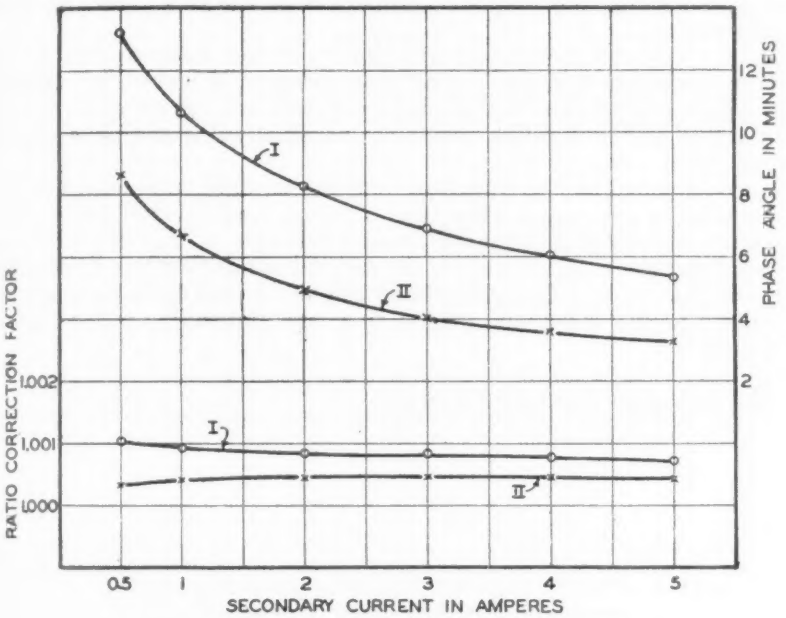


FIGURE 18.—*Performance curves for transformer* G_4.

Hole type. Circular core. Secondary winding uniformly distributed around the core. Nominal ratio $\frac{5000}{5}$. Burden 0.8 ohm and 1,000 microhenries. Frequency 25 cycles per second.

Curve	Arrangement of primary circuit
1	Straight conductor through center of core window, four return leads equally spaced around inner conductor and 20 inches from it.
2	A loop, 12 inches in diameter, of large cable around a section of the core.

The results of the experiments on these two transformers indicate that the performance of transformers of this design is nearly independent of the arrangement of the primary circuit. Arnold [5] has shown that this is not the case for certain transformers with cores made of a nickel-iron alloy, designed for 5,000 ampere-turns or over. With a concentrated primary winding these transformers showed very large errors, which could probably be materially reduced by the use of a

[5] A. H. M. Arnold, Leakage phenomena in ring-type current transformers. J.Inst. Elec. Engrs. (London) 74, 413 (1934).

silicon-steel core, since silicon-steel reaches its maximum permeability at a much higher flux density than the nickel-iron alloys. However, it must be concluded from Arnold's paper, that for ring-core transformers of over 5,000 ampere-turns, the arrangement of the primary circuit may have an appreciable effect on performance.

V. CONCLUSIONS

1. The more uniformly the secondary winding of a current transformer is distributed around its core, the less will changes in arrangement of primary circuit affect the performance.

2. The actual changes in ratio and phase angle for a given change in location of the primary circuit depend not only upon the shape of the core and distribution of secondary winding, but also upon the core dimensions, the magnetic properties of the core, and the rated ampere-turns.

3. A symmetrical location of primary circuit with respect to the core is generally the best for all transformers; however, in some instances, concentration of the primary circuit around a certain section of the core will give ratios nearer the nominal value and phase angles nearer zero.

4. With a primary circuit consisting of a straight conductor through the center of the core window and a return lead divided into several sections uniformly distributed around the core, a change in the distance from the return leads to the central conductor has little effect on performance. The performance will also be nearly the same when several primary turns are used if they are uniformly spaced around the core.

WASHINGTON, January 25, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP776

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

STANDARD CONDITIONS FOR PRECISE PRISM REFRACTOMETRY

By Leroy W. Tilton

ABSTRACT

Air as a standard reference medium for precise refractive-index measurements is discussed with respect to the precision necessary in the control and measurement of its temperature, pressure, humidity, and carbon-dioxide content. Particular attention is given to the selection of provisional values for α, the optical temperature coefficient for air; and the preparation of accurate correction tables for the reduction of refractive-index observations to standard conditions of reference is described and exemplified.

The approximate range of temperature effects on absolute refractive index is indicated; also the range of pressure effects on liquids. A new (empirical) relation between index and density is derived from Pockels' optical data on elastically deformed glass and a basis for quantitative treatment of permissible stress-birefringence is given. For glasses, the character of annealing and the permissible degree of striation are considered; and for several media the requisite constancy in wave length of light source is determined.

Tolerance equations are given for all requirements that are quantitatively discussed and it is concluded that both precision and accuracy to within ± 2 or 3×10^{-6} can be attained in determining refractive index by the classical method of minimum deviation.

CONTENTS

	Page
I. Introduction	394
II. Air as a standard medium of reference	396
1. Tolerances in measurement and control of reference medium	397
(*a*) Temperature of air	399
(*b*) Pressure of air	400
(*c*) Humidity of air	400
(*d*) Carbon-dioxide content of air	402
2. Corrections to standard reference conditions	403
III. Requisite constancy and uniformity for refractive media	406
1. Effects of temperature on refractive media	407
(*a*) Thermal coefficients of absolute refractive index	407
(*b*) Approximate range in temperature tolerances for solids and liquids	408
2. Effects of pressure on refractive media	409
(*a*) Variations in atmospheric pressure	410
(*b*) Stress and birefringence	412
3. Heat treatment, chemical heterogeneity, and striation of glass	414
IV. Requisite precision in source of radiation	415
V. Precision and accuracy attainable in minimum-deviation refractometry	416

I. INTRODUCTION

In the practice of precise refractometry a desirable degree of approximation to the ideal physical and chemical conditions of measurement is seldom realized. Although the necessity for control of some of the physical conditions is more or less well known, only a comparatively small amount of the published index data is accompanied by adequate references to the conditions under which the measurements were actually made or to the conditions which are considered as standard.[1]

The tolerances for variations in air temperature, pressure, and humidity have not been explicitly and precisely evaluated, and the effects of temperature and pressure on the absolute indices of various media are not adequately known. Moreover, the question of the effect of heterogeneities in the sample has not hitherto been discussed in connection with refractive-index measurements. On the other hand, it appears that no attempt has been made to justify or to disprove the commonly accepted opinion that even a moderate amount of birefringence in a medium may make precise index measurements useless.

Certain refractive-index measurements of high precision, that are being made in the refractometric laboratory at the National Bureau of Standards, have made it necessary to determine the precision with which all of the working conditions must be controlled or, in some instances, quantitatively observed. It has seemed advisable to differentiate clearly between the effects of such conditions on the reference medium and on the sample to be measured and, wherever possible, to specify on a quantitative basis the requirements and tolerances relating to these working conditions; also, to set forth in detail a system of accurate corrections to standard reference conditions. However, when considering such matters as heterogeneity of the sample and the permissible degree of its birefringence, the treatment is necessarily limited to simple approximations.

For convenience of reference, the definitions of various symbols that are used and explained in this paper are summarized here as follows:

$\alpha \equiv$ temperature coefficient of expansion of air at constant pressure; also (negative) temperature coefficient of refractivity;

$\beta \equiv$ pressure coefficient of volume change at constant temperature (often called compressibility), that is

$\beta = -\frac{1}{V_0}\left(\frac{dV}{dP}\right)$; also, for air, the pressure coefficient of refractivity;

$C \equiv$ total (volume) proportion of CO_2 in atmosphere;

$C', C'', C''' \equiv$ constants of proportionality in various equations expressing index-density relationship;

$c \equiv$ excess of CO_2 above the normal proportion, that is, $c = C - 0.00035$;

$d \equiv$ density;

[1] Brief historical references have been made in a former paper, BS J. Research 2, 912-915 (1929) RP64.

$E \equiv$ Young's modulus of elasticity;
$\epsilon = 179 \times 10^{-6}/(\mu_o - 1)$;
$\gamma = 41 \times 10^{-6}/[760(\mu_o - 1)]$;
$K \equiv$ modulus of volume elasticity or "bulk modulus", that is, $K = 1/\beta$;
$\lambda \equiv$ wave length of light;
$m \equiv$ mass;
$\mu \equiv$ index of refraction of air, the general subscripts t, p, v, and c referring to the temperature, pressure, humidity, and carbon-dioxide content, respectively, while the subscript 0 indicates standard conditions of 0° C and 760 mm pressure and D specifies a wave length of 5893 A;
$n \equiv$ relative (to air) index of refraction of a medium;
$\bar{n} \equiv$ absolute (or vacuum) index of refraction of a medium;
$P \equiv$ pressure of air;
$p \equiv$ excess in mm of Hg over 1 atmosphere of air pressure, that is, $p = (P - 760)$;
(p'/v') and $(q'/v') \equiv$ the Pockels experimental constants for certain glasses, v' being the velocity of light in the unstressed glass;
$s \equiv$ proportion by volume of striae in glass;
$\sigma \equiv$ Poisson's ratio;
T and $t \equiv$ temperatures on absolute and centigrade scales, respectively;
$T_{\Delta t_a} \equiv$ tolerance in air temperature control and measurement that corresponds to an error of $\pm\ 1 \times 10^{-6}$ in (relative) refractive index;
$T_{\Delta p_a} \equiv$ tolerance in air-pressure control and measurement that corresponds to an error of $\pm\ 1 \times 10^{-6}$ in (relative) refractive index;
$T_{\Delta v} \equiv$ tolerance in absolute humidity that corresponds to an error of $\pm\ 1 \times 10^{-6}$ in (relative) refractive index;
$T_{\Delta c} \equiv$ tolerance in abnormal proportion (by volume) of CO_2 in the atmosphere that corresponds to an error of $\pm\ 1 \times 10^{-6}$ in (relative) refractive index;
$T_{\Delta P} \equiv$ tolerance in hydrostatic-pressure variations corresponding to $\pm\ 1 \times 10^{-6}$ in refractive index of liquid and solid media;
$T_{\Delta n_b} \equiv$ tolerance in absolute stress-birefringence corresponding to an error of $\pm\ 1 \times 10^{-6}$ in refractive index (for the transverse ray if $n < 1.8+$);
$T_{\Delta\lambda} \equiv$ tolerance in wave length of source corresponding to an error of $\pm\ 1 \times 10^{-6}$ in refractive index;
$V \equiv$ volume; and,
$v \equiv$ pressure of water vapor in the atmosphere in mm of Hg.

II. AIR AS A STANDARD MEDIUM OF REFERENCE

The great majority of all measurements involving light velocities are made while using the earth's atmosphere as the practical standard medium of immersion or reference. Since the velocity of light in air is a function of chemical composition and also of the temperature and pressure of air, it is necessary to specify CO_2, moisture content, and other factors with appropriate precision in order that the measurements may have definite value.

The composition of CO_2-free dry air has been discussed in a former paper.[2] Although this composition appears constant to a high degree when air is chemically analyzed, it has long been estimated that variations in the normal density of air are as large as 5 or 10 parts in 10,000 and for this reason air is no longer considered a suitable reference medium for accurate specific gravities of gases. Statistical analysis of existing data indicates, likewise, that the refractive index of air at standard conditions is not constant but varies over a range perhaps as large as $\pm 12\times10^{-7}$ from a general average value of 1.0002925 for $\lambda=5893$ A. Consequently all relative indices of refraction may be subject to an inherent uncertainty which can be estimated as

$$\Delta n=\pm 12n\times10^{-7} \tag{1}$$

unless accompanied by reliable measurements on air itself.

In reducing relative indices to absolute values when direct measurements on air are lacking, it is probable that this uncertainty is statistically diminished by using for μ, the index of air, a value properly computed [3] from dispersion data and from an equation that gives the sodium-lines index of air for 0° C and 760 mm pressure as

$$(\mu_D-1)\times10^7=\mu_{S=0}-kS \tag{2}$$

where S is the relative annual sunspot number (for the year in which the relative indices were measured) as given in the Wolf-Wolfer series of sunspot observations. For use in this equation the parameters $\mu_{S=0}$ and k should be determined from the best available data on the refractive index of air for the period in question. Provisional values obtained by the writer for the whole interval 1857 to 1934 are, respectively, 2932.2 and 0.148; whereas for the limited interval 1912 to 1934, during which a number of very important observations have been made, the corresponding values of the parameters are 2927.5 and 0.079. With either of these sets of values for the parameters, however, the probable errors of estimates of index interpolated by use of equation 2 are large, namely ±5 and $\pm3\times10^{-7}$, respectively, and it is readily seen that for certain years within the interval 1912 to 1934 two estimates can actually differ by 5×10^{-7}. Extrapolations will probably be even less reliable and consequently it appears (see equation 1) that uncertainties of ±1 or 2 units of the sixth decimal place of index can not be entirely excluded when refractivities of optically dense media are measured in CO_2-free dry air. From evidence at present available it does not seem likely, however, that such differences can occur over periods of time measured in days or weeks but rather that such possibilities should be remembered when comparing absolute determinations separated by or extending over a period of years.

[3] L. W. Tilton, BS J. Research 13, 111 (1934) RP695.
[2] See equation 22 of this paper.

Obviously, it is seldom convenient to use as a reference medium pure air having a standard temperature and pressure, and free from CO_2. Usually it is advisable to allow these conditions to vary continuously and to keep adequate records during index determinations. In investigating the relationships involved, a unit error of 1×10^{-6} will be considered as was done in former papers [4] discussing the geometrical aspects of prism refractometry.

1. TOLERANCES IN MEASUREMENT AND CONTROL OF REFERENCE MEDIUM

The most obviously important effects of varying air conditions on measured relative indices are those arising from the changes in air density through changes in pressure, P, and in air temperature, T (absolute). The relationship between the index of air and its density, d, is usually assumed to be that constancy expressed by Gladstone and Dale's law as $(\mu-1)=Cd$. Then, in accordance with the ideal gas law, $PV=RT$, it is customary to write for any given wave length

$$(\mu-1)_{TP}=(\mu_0-1)\left(\frac{273}{760}\right)\left(\frac{P}{T}\right) \tag{3}$$

where μ_0 is a value for standard conditions of 0° C and 1 atmosphere pressure, and P is measured in mm of Hg; or, defining p as the excess in mm of Hg over 1 atmosphere of pressure, $p=(P-760)$ and

$$(\mu-1)_{tp}=(\mu_0-1)\frac{(1+\beta p)}{(1+\alpha t)} \tag{4}$$

where t is the temperature on the centigrade scale, β is the pressure coefficient of volume change of a gas at constant temperature (namely 1/760 for a 1 mm change at a pressure of one atmosphere) and α is the temperature coefficient of expansion of air at constant pressure. The value of α would be $0.00366=1/273$ for a change of 1° C, at a temperature of 0° C, if air behaved like a perfect gas, but 0.00367 if the results of experiments on the expansion of air are considered. The only published references to computed reductions or corrections for indices measured in air at other than standard conditions have been based on these or on similar assumptions.

Since at constant temperature the proportionality between $(\mu-1)$ and d has been found to hold without serious discrepancy over a pressure range of many atmospheres, it is safe to assume that the pressure coefficient of refractivity is identical with β for such small variations in atmospheric pressure as those which occur during index measurements and also, for variations which exist between various places on the earth's surface. Concerning α, however, the similar assumption does not seem equally reliable. According to generally accepted theories of dispersion, a change in the temperature of a medium affects the resonance frequency as well as the mass per unit volume. As a result there is a change or "shift" of the effective wave length of the absorption band, and for each given wave length a different secondary temperature influence on index is superposed on that which is directly ascribed to the change in density. Thus it is

[4] L. W. Tilton, BS J. Research **6**, 59 (1931) RP262; **11**, 25 (1933) RP575.

not necessarily true that values of $\partial \mu/\partial t$ can be accurately obtained by differentiating equation 4 with respect to t and solving for

$$\frac{\partial \mu}{\partial t} = -\frac{\alpha(\mu-1)_{tp}}{1+\alpha t} \tag{5}$$

with a constant value of α determined from the expansion of air or even from index data for a single wave length. Instead of such a constant "optical temperature coefficient",[5] the measurements on air by W. F. Meggers and C. G. Peters [6] yield an α varying with wave length from 0.00367_4 at 7500 A to 0.00373_8 at 3500 A.

Table 1 summarizes the results of direct determinations of this constant for air. The Gylden value was deduced from astronomical observations. Mascart's value should not be considered because of a systematic inconsistency in results obtainable from his data.[7] Scheel's

TABLE 1.—*Optical temperature coefficient for air*

(Visible range of frequencies)

Observer	Reference	Temperature interval on Centigrade scale	$\alpha \times 10^4$
Gylden	Mém.acad.St.Petersburg **10,** no. 1 (1866); **12,** no. 4 (1868)	Seasonal range	369
L. Lorentz	K.Danske Videnskab.Selskabs Skrifter [5] **10,** 485 (1875)	1 to 17°, 100°	367
Von Lang	Pogg.Ann. **153,** 463 (1874). (This α is given as computed by Benoit).	2 to 95°	303
Mascart	Compt.Rend. **78,** 617–679 (1874); Ann.Sci.École Normale Supérieure [2] **6,** 9–78 (1877).	5 to 38°	382
Benoit	Travaux et Mémoires Bur. Int. Poids et Mesures **6,** 102 (1888).	1 to 80°	367
Walker	Trans.Roy.Soc. (London) **A201,** 454 (1903)	10 to 100°	369
Scheel	Verhandl.deut.physik.Ges. **9,** 24–36 (1907)	−192 to 0°	373
Barus	Carnegie Inst.Wash.Pub.no. 249–I, page 137 (1916)	22 to 100°	361
Meggers and Peters	See page 735 Bul BS **14,** (1918) S327	0 to 30°	368_8
Pérard	J.phys.radium [6] **6,** 223 (1925)	0 to 100°	371_4
Cheney	Phys.Rev. [2] **29,** 292–298 (1927)	25 to 300°	367

α is very high, but his temperature interval is much lower than that used by the others. He selected $\alpha=0.00367_4$ for reducing his own index of air from 16 to 0° C. Cheney's temperature interval is much higher than that used by the others. A close analysis of his published numerical data shows that a low value of $\alpha=0.00364$ fits as well or better than the conventional value which he considered verified. Von Lang's α is too low for serious consideration and no great accuracy was claimed for the Barus data.[8]

Considering the amount of data taken, particularly the number of temperatures used, the results by Benoit and by Pérard are probably entitled to special consideration. They used the same method (Fizeau dilatometer) and to some extent the same apparatus. If their values are averaged one has $\alpha=0.00369$ which agrees closely with the average value of $\alpha=0.00368_8$ that is obtained from the Meggers

[5] From inspection of equation 5 one finds that α can be regarded as the (negative) temperature coefficient of index of refraction of air per unit of "excess refractivity", as determined for $t=0°$ C and $p=0$.

[6] Bul. BS **14,** 697 (1918) S327.

[7] If from the experiments which he conducted when investigating temperature effects one discards those for temperatures below the middle group, which averages 14.4° C for t, the writer finds that $\alpha=0.00395$ is indicated. On the other hand, when the observations at temperatures above those of the middle group are discarded an $\alpha=0.00356$ is obtained.

[8] It is of interest to note that Barus' qualitative conclusion concerning the decrease of α for high temperatures is consistent with the trend which has been mentioned for some of the data of table 1, particularly the high value which Scheel found in the very low temperature interval that he used, and the low value which the writer would recommend from Cheney's data.

and Peters data for those particular wave lengths [9] which Pérard used. Thus it seems certain that the optical temperature coefficient is appreciably larger than the coefficient of expansion which has been so generally used. Since the Meggers and Peters values of α are based on data for such a large number of wave lengths, and since their average for the visible region is in excellent agreement with the average α from the Benoit and the Pérard data, the Meggers and Peters values are therefore recommended for all intercomparisons between precise relative-index data taken at markedly different temperatures.

The wave-length variation in α is of importance chiefly in the ultraviolet region; but even for the visible region, especially for the shorter wave lengths, it is in some cases preferable to use the variation in α when reducing six- and seven-decimal-place indices to certain reference conditions. In particular, when relative indices are used as a basis for computing temperature variations in the absolute index of a medium, it is desirable to consider the most accurate data available on air.

(a) TEMPERATURE OF AIR

Whether α is regarded as constant or as varying with wave length, a formal expression for the error in relative index caused by air-temperature variations is readily written after considering the definitive relation

$$n \equiv \frac{\bar{n}}{\mu} \tag{6}$$

which exists between the relative index, n, of a medium and its absolute index, $\bar{n}$. Since the latter is necessarily independent of air temperatures and μ^2 is approximately unity

$$\frac{dn}{dt} = -\bar{n}\frac{d\mu}{dt} \tag{7}$$

and consequently, using equation 5, it is found that changes in air temperature result in index variations of like sign according to the equation

$$\Delta n = \frac{\bar{n}\alpha(\mu-1)_{tp}}{(1+\alpha t)}\Delta t_a \tag{8}$$

from which precise index corrections may be computed for the whole wave-length interval 2218 to 9000 A by using the Meggers and Peters values [10] of α, which they approximately expressed by the equation

$$\alpha = 0.00367 + \frac{3\times10^{-6}}{\lambda^3} \tag{9}$$

where λ is to be used in microns.[11]

For the purpose of establishing practical tolerance limits in temperature control and measurements, $\bar{n}$ is essentially equivalent to n, and α for the visible region is approximately the ratio 1/270. Moreover, it happens that the refractivity of air at temperatures between 0 and 50° C varies only from about 24 to 30×10^{-5} over the range of

[9] Pérard used only five wave lengths, all within the visible region, and the data do not seem sufficiently concordant either to confirm conclusively or to disprove the variation of α with wave length.

[10] See page 735 Bul. BS **14** (1918) S327.

[11] For precise refractometry the angstrom is generally favored by the writer as the appropriate unit of wave length, but the micron is often more convenient in the writing and using of dispersion equations.

the visible spectrum, and ordinary atmospheric-pressure changes of $p=\pm 30$ mm do not materially increase this variation. Therefore, with an accuracy of approximately $\pm$ 10 percent, the tolerance corresponding to $\pm 1\times10^{-6}$ in refractive-index measurement is

$$T_{\Delta t_a}=\pm n^{-1}(1+\alpha t) \text{ degrees C} \tag{10}$$

or, for work on media having indices of 1.9 and 1.3, respectively, the air-temperature changes of $\pm 0.53°(1+\alpha t)$ and $\pm 0.77°(1+\alpha t)$ are equivalent to errors of $\pm 1\times10^{-6}$ in the measured relative indices. Thus it is evident that a neglect of seasonal changes in air temperatures may easily affect the fifth decimal place of relative-index work on any medium, even though its temperature coefficient of absolute index is negligibly small.

(b) PRESSURE OF AIR

For the purpose of arriving at similar correction and tolerance equations for air pressures, one differentiates equations 4 and 6 with respect to p and finds that an increase in air pressure results in a decreased value of the measured relative index of other media according to the equation

$$\Delta n=-\frac{\bar{n}\beta(\mu-1)_{tp}}{(1+\beta p)}\Delta p \tag{11}$$

from which precise corrections to measured indices can be satisfactorily computed.

Again approximating, as was done with equation 8, equation 11 reduces to the practical working tolerance in air pressures

$$T_{\Delta p_a}=\pm 2.8n^{-1}(1+\beta p)\text{mm} \tag{12}$$

which is written for an error of $\pm 1\times10^{-6}$ in refractive index and, obviously, for the usual small values of p only one term is needed. Thus for media having indices of 1.9 and 1.3, respectively, the air-pressure changes of 1.5 and 2.2 mm are equivalent to variations of unity in the sixth decimal place of measured relative index of refraction. For many localities, therefore, it is apparent that the fluctuations in barometric pressure within a single working day should not be neglected in precise measurements of relative index, and it is certain that the air-pressure variations that occur over somewhat longer periods affect the fifth decimal of such indices.

(c) HUMIDITY OF AIR

The proportion of water vapor in air is such a variable factor, depending on locality and weather conditions, that it is a difficult matter to decide upon any definite proportion as a satisfactory normal moisture content of the atmosphere. Consequently it is probably better to treat moisture as an impurity and refer all refractive-index measurements to dry air as a standard reference medium.

L. Lorenz [12] gives, for sodium light, a value of $\mu_D=1.0002500$ as the index of refraction of water vapor at a concentration of 1 mol in 22.4 liters. Comparing this with his index of dry air for equivalent conditions, he gives a correction of $\Delta\mu_v=-0.000041\ v/760$ to be applied to his results on dry air when it is desired to obtain indices for moist

[12] Ann. Physik [3] **11**, 91 (1880).

air containing water vapor of v mm pressure. The Cuthbertsons [13] and others [14] have confirmed the magnitude of this correction and, for the region 4779 to 6708 A, have shown that the dispersion of water vapor is closely comparable with that of air. It seems, in fact, from experimental evidence, that the coefficient of this Lorenz correction, namely, 41×10^{-6}, should not vary more than $\pm 1 \times 10^{-6}$ throughout the visible spectrum.

Since the pressure of water vapor in the air seldom exceeds a small fraction of an atmosphere, it seems permissible to assume the equivalence of optical temperature coefficients for water vapor [15] and for air, and to use the Lorenz humidity correction for all ordinary temperatures by writing for the whole visible range of frequencies

$$(\mu_t - 1)_v = (\mu_t - 1)_{v=0}(1 - \gamma v) \tag{13}$$

where $\gamma = 185 \times 10^{-6}$ is used to replace $41 \times 10^{-6}/[760\ (\mu_0 - 1)]$. This equation is written for a pressure of 760 mm, but is applicable at all ordinary atmospheric pressures. Differentiating equation 13 with respect to v gives

$$\frac{d\mu}{dv} = -\gamma(\mu_t - 1) \tag{14}$$

and, referring to a similar differentiation of equation 6, it is evident that an increase in the moisture content of the air results in an increased relative index of a medium which is being measured therein, the error equation being

$$\Delta n = +\bar{n}\gamma(\mu_t - 1)\Delta v \tag{15}$$

for use in precise computations of refractive index of the medium which is measured in air.

For an error of unity in the sixth decimal of index, and with sufficient accuracy for many purposes, equation 15 yields

$$T_{\Delta v} = \pm\ 20n^{-1}\text{mm} \tag{16}$$

which shows that the unit tolerances in absolute humidity vary from approximately $\pm$ 10 to $\pm$ 15 mm of vapor pressure. These figures apply to measurements of relative index on media having indices of 1.9 and 1.3, respectively. Vapor pressures of 10 and 15 mm correspond at 50° C to 10 and 15 percent in relative humidity and at 30° C to 30 and 45 percent, respectively. Thus it is evident that humidity corrections are not negligible in sixth-decimal-place refractometry, especially when working in air at temperatures somewhat higher than those of ordinary room conditions or whenever there is danger of humidities approaching the saturation point (because, for example, of leaks in water-jacketed housings used for temperature control).

[13] C. and M. Cuthbertson, Trans. Roy. Soc. (London) A**213,** 16 (1913).

[14] J. Wüst and H. Reindel, Z. physik. Chem. B**24,** 176 (1934). See, also, P. Hölemann and H. Goldschmidt, page 204 of same volume.

[15] From the Hölemann and Goldschmidt data (see footnote 14) on water vapor, considered together with published densities of steam, one may deduce a tentative value $\alpha = 0.0035$ to compare with 0.0037 for air.

(d) CARBON-DIOXIDE CONTENT OF AIR

After water vapor the next atmospheric constituent of recognized importance, so far as its variability is concerned, is carbon dioxide. Although the range in its fluctuations is known to be much smaller than in the case of water vapor, there is a prevalent opinion that when using air as a reference medium for measurements of highest precision one should eliminate either the CO_2 itself or the effects of its variations. While there are on record some presumably reliable analyses of air showing a carbon-dioxide content as high as 0.3 percent by volume, such samples were taken under exceptional circumstances, such as in very crowded theaters of an obsolete and most unfavorable type, or in rooms with no ventilation, and they have no interest in the present connection. Boothby and Sandiford [16] reported that outdoor air sampled under favorable conditions varies in its CO_2 content by only a few thousandths of one percent from a normal value of 0.036 percent. Similarly, F. G. Benedict [17] found that outdoor air does not vary in this respect more than a few thousandths from an average value of 0.031 percent, but Hann [18] states that the percentage of CO_2 varies from 0.033 to 0.043 in the air of cities. Consequently, in view of these small variations, it seems permissible and somewhat preferable to adopt some value, say 0.00035, as the normal volume proportion of CO_2 in air rather than to favor the more stringent requirement that a standard reference medium must be entirely free from carbon dioxide.

Precise index measurements are, of course, seldom made in outdoor air, but in any well ventilated modern laboratory it is unlikely that the carbon-dioxide content ever exceeds two or three times the normal value. In air from the Boston and New York subways, sampled just after the rush hours, Benedict found only twice the normal CO_2 content. Moreover he found that an increase in CO_2 is accompanied by an equal volume decrease in O_2, and consequently it is the difference in the refractivities of carbon dioxide and of oxygen which must be considered in making corrections to indices measured in air having an abnormal CO_2 content.

The averages of a number of published [19] values of the refractive indices of CO_2 and O_2 are 1.000450 and 1.000271, respectively, for sodium light, a temperature of 0° C and a pressure of 760 mm. Hence a correction of

$$\Delta\mu_C = +0.000179(C-0.00035) \tag{17}$$

should be applied to the measured index of normal air (containing the proportion 0.00035 of CO_2) at 0° C and 760 mm pressure when it is desired to obtain the index of air containing the total proportion C of carbon dioxide.

A comparison of the dispersions of oxygen and of carbon dioxide shows that the correction given by equation 17 varies only 1 percent or less for the visible-spectrum region. Proceeding as with the water-vapor correction (part c of this section) and writing $c = C - 0.00035$ to represent excess CO_2, one finds for all ordinary temperatures

$$(\mu_t - 1)_C = (\mu_t - 1)_{c=0}(1+\epsilon c) \tag{18}$$

[16] Am. J. Physiol. **55**, 295 (1921).
[17] The Composition of the Atmosphere, Carnegie Inst., Wash., Pub. no. 166., pages 110–114 (1912).
[18] J. von Hann's Lehrbuch der Meteorologie, page 5 (1915).
[19] See Landolt-Börnstein Tabellen.

where $\epsilon = 0.612$ replaces $179 \times 10^{-6}/(\mu_0 - 1)$. Differentiating equation 18 with respect to c gives

$$\frac{d\mu}{dc} = +\epsilon(\mu_t - 1) \tag{19}$$

whence, again using equation 6, it is apparent that the presence in laboratory air of CO_2 in abnormally high proportions results according to the equation

$$\Delta n = -\overline{n}\epsilon(\mu_t - 1)\Delta c \tag{20}$$

in decreased values for such relative indices as are measured in the laboratory.

For unit error in the sixth decimal place of refractive index the corresponding tolerance in volume proportion of abnormal CO_2 content of air is

$$T_{\Delta c} = \pm\ 0.006n^{-1} \tag{21}$$

with sufficient accuracy for all purposes. Evidently no consideration whatever need be given to CO_2 content of air in sixth-decimal-place refractometry. Even for the extreme case when a medium of index 1.9 is being measured, the excess proportion of CO_2 must reach the high value of 0.003, or nine times the proportion normally present in fresh air, in order to produce an error of -1×10^{-6} in relative index. For seventh-decimal-place index work, however, it may be ascertained from these results that the normal CO_2 content of fresh air causes a lowering of approximately 1×10^{-7} in the measured relative indices of very dense media as compared with the use of a standard reference air containing no carbon dioxide. Consequently, it may be safely inferred that, in general, indices of laboratory air, or relative indices measured in such air, are not likely to have any precision whatever in the eighth decimal place unless simultaneous CO_2 determinations are made.

2. CORRECTIONS TO STANDARD REFERENCE CONDITIONS

If the working conditions affecting the reference medium are not maintained constant at the desired standard values or controlled within the tolerance limits as specified above, then it becomes necessary to observe the existing conditions and make the proper corrections to the results actually obtained. When it is necessary to correct sixth-decimal-place indices to standard conditions, or to convert them to absolute indices, the use of slide-rule corrections is often lacking in adequate precision and correction tables for these purposes are advisable. Their preparation in detail is a profitable preliminary whenever numerous data are to be reduced for a limited number of spectral lines. For highest precision such tables are especially desirable because certain refinements in precision of correction need be considered explicitly only during their original preparation.

The writer recommends the use of logarithms in the computation of indices, and the evaluation of all corrections in terms of log n. One of the first requirements is a double-entry table of barometer corrections with barometer temperature and barometer reading as arguments. With the temperature reductions [20] to be listed in this table the barometer calibration corrections (for a given instrument)

[20] Temperature reductions for use with a Fortin-type barometer and brass scale are given in tables 46 and 47 of the 4th revised edition, Smithsonian Meteorological Tables.

are combined and then all entries are modified to reduce pressures from local [21] to standard gravity, $g=980.665$ dynes.

Another requirement is a series of double-entry tables (or their equivalent), with air pressure and temperature as arguments, giving the positive corrections which, when applied to log n, will yield log $\bar{n}$, of which the antilog is absolute index. The various members of such a series of tables relate to the different spectral lines that are to be frequently used for index measurement and these member tables will differ principally because of the dispersion of air. (There is also a slight additional difference because of the nonconstancy of α, the optical temperature coefficient of index. See discussion in part 1 of section II.) As an example of a member table of such a series, table 2 is abstracted (by decimation in each argument) from a usefully detailed tabulation for the hydrogen line, $\lambda=4861$ A.

TABLE 2.—*Data for converting from relative to absolute index* ($\lambda=4861$ A) *by the equation* $\log \bar{n}=\log n+\log \mu$

P=air pressure (in mm of mercury)	Values of $10^8\times\log \mu_P$ for dry air at various temperatures (with normal CO_2 content)				
	0° C ($\Delta P=0.06$)	10° C ($\Delta P=0.13$)	20° C ($\Delta P=0.24$)	30° C ($\Delta P=0.44$)	40° C ($\Delta P=0.77$)
730	12295	11857	11449	11069	10713
740	12464	12020	11606	11220	10859
750	12632	12182	11763	11372	11006
760	12800	12344	11920	11524	11153
770	12969	12507	12077	11675	11300
780	13137	12669	12234	11827	11446

NOTES

1. For each 10 percent of relative humidity subtract tabulated values of ΔP from air pressure before entering this table.
2. Tentatively it may be advisable to reduce log μ by 5 or 10 parts in 10,000 for each increase of 20 in relative annual sunspot number above average $S=46$.
3. If it is desired to use these data for wave lengths other than 4861 A, modify air temperature according to table 4 before entering this table.

In preparing such correction tables in this laboratory, the temperature and dispersion data as given by Meggers and Peters [22] have been combined with the average value of refractive index, $\mu=1.0002926$ (for $\lambda=5893$ A, $t=0°$ C and $P=760$ mm), which is obtained by considering all published data [23] and adding a very slight correction for normal CO_2 content. Since the ratio of log μ to $(\mu-1)$ is very nearly constant over the whole range in μ that is involved in temperature and pressure reductions and corrections, the actual computation of air indices is unnecessary except for 0° C and 760 mm pressure. The values of log μ for all ordinary temperatures and pressures may be directly computed (see equation 4 and citations of footnote 22) from the equation

$$\log \mu_{tp}=\frac{1+\beta p}{1+\alpha t}\log\left[1+\left(2884.3+\frac{13.412}{\lambda^2}+\frac{0.3777}{\lambda^4}\right)\times 10^{-7}\right] \quad (22)$$

where α varies with wave length as approximately expressed by equation 9, and λ should be written in microns.

[21] Gravity reductions are discussed on pages XXXV and XXXVI of 4th revised edition, Smithsonian Meteorological Tables.
[22] See pages 722 and 735, Bul. BS 14 (1918) S327.
[23] See page 115, BS J. Research 13 (1934) RP695.

If, in table 2, the values for a standard pressure are subtracted from those for other pressures in the same column, a set of air-pressure corrections to the logarithms of observed indices is obtained. Table 3 gives such corrections for limited ranges in pressure and in temperature variations. Such a table may, of course, be computed directly from the basic values of the logarithms for the indices at standard pressure, $p_0=760$ mm. For this purpose the equation

$$\Delta \log \mu_{tp}=\frac{\log \mu_{tp_0}}{760}\Delta p \qquad (23)$$

is obtained from equation 22.

TABLE 3.—*Data for referring relative indices to dry air at standard pressure by the equation* $\log n_{760}=\log n_p+\Delta\log n$.

Use tabulated values with negative sign when $P-760$ is negative]

($P-760$ mm) ≡ excess atmospheric pressure	Values of $10^8 \times \Delta \log n$ for various air temperatures		
	10° C ($\Delta P=0.13$)	20° C ($\Delta P=0.24$)	30° C ($\Delta P=0.44$)
20	325	314	303
19	309	298	288
18	292	282	273
17	276	267	258
16	260	251	243
15	244	235	227
14	227	220	212
13	211	204	197
12	195	188	182
11	179	173	167
10	162	157	152
9	146	141	136
8	130	125	121
7	114	110	106
6	97	94	91
5	81	78	76
4	65	63	61
3	49	47	45
2	32	31	30
1	16	16	15
0	0	0	0

NOTE.—For each 10 percent of relative humidity subtract tabulated values of ΔP from air pressure before entering this table.

Although the direct use of table 2 is strictly limited to the correction of indices for the F line of hydrogen, table 3 is applicable over a very wide range in the spectrum. In fact, for pressure corrections as large as 30 mm the use of table 3 may be extended over the whole visible range of frequencies without errors exceeding $\pm$ 5 x 10^{-8} in the logarithmic corrections so determined.

As they are written, tables 2 and 3 both relate to dry air and must be modified because of the presence of water vapor. From equations 11 and 15 it is evident that any given increase in moisture can be represented as an equivalent decrease in pressure, and thus it is possible to find a simple system of modifying the actual corrected pressures to fictitious or pseudo pressures which, when used as actual pressures, permit tables 2 and 3 to serve for moist as well as dry air. Hence the ΔP equivalents which appear in the column headings of tables 2 and 3.

If for any reason it is objectionable to prepare a complete series of log μ tables, similar to the single example given as table 2, one may use a relationship between $\Delta\mu/\Delta\lambda$ and $\Delta\mu/\Delta t$ for extending to other wave lengths the use of a table written primarily for one particular

TABLE 4.—*Auxiliary data for extending use of table 2 to various wave lengths*

$\lambda \equiv$ wave length (in angstroms)	Values of Δt for modification of air temperatures		
	0° C	20° C	40° C
4000	−3.18	−3.30	−3.43
4100	−2.70	−2.80	−2.91
4200	−2.25	−2.33	−2.42
4300	−1.83	−1.90	−1.98
4400	−1.45	−1.50	−1.56
4500	−1.10	−1.14	−1.18
4600	−0.76	−0.79	−0.82
4700	−0.45	−0.47	−0.49
4800	−0.16	−0.17	−0.18
4900	+0.11	+0.11	+0.12
5000	+0.36	+0.38	+0.40
5200	+0.81	+0.84	+0.87
5400	+1.21	+1.26	+1.31
5600	+1.57	+1.63	+1.69
5800	+1.88	+1.96	+2.04
6000	+2.17	+2.26	+2.35
6200	+2.42	+2.52	+2.63
6400	+2.65	+2.76	+2.88
6600	+2.86	+2.98	+3.10
6800	+3.05	+3.18	+3.31
7000	+3.21	+3.36	+3.50

wave length. For this procedure it is found advantageous to regard temperature as the fictitious argument, and table 4 gives the particular corrections of this type that should be algebraically applied to actual air temperatures before entering table 2 for wave lengths other than 4861 A.

III. REQUISITE CONSTANCY AND UNIFORMITY FOR REFRACTIVE MEDIA

Uniformity of reference conditions is a necessary but by no means a sufficient condition for high precision in refractometry. Even the absolute indices of refraction of optical media are ratios which may, for divers reasons, vary from time to time or with respect to coordinates within the media. Temperature and pressure are obviously important factors and, in the case of optical glass, heat treatment may introduce not only a variation of index with direction of travel of the light, but also a marked physico-chemical change [24] in index that often varies from point to point in the glass although it is not a function of orientation. Moreover, the writer has found that striae in glass, when they exist in well-stratified layers, can affect measurements of index and of dispersion in a systematic manner that may prove misleading in some investigations. Therefore, for consistent results in index determinations, it is necessary carefully to consider the conditions which cause real or apparent changes in the optical density of media that are subject to measurement.

[24] A. Q. Tool and C. G. Eichlin, J.Opt.Soc.Am. **4**, 359 (1920); BS J.Research **6**, 525 (1931). A. Q. Tool, L. W. Tilton, and E. E. Hill, J.Opt.Soc.Am .and Rev.Sci.Inst. **12**, 490–491 (1926). L. W. Tilton, J.Wash' Acad.S ci. **20**, 12–13 (1930).

1. EFFECTS OF TEMPERATURE ON REFRACTIVE MEDIA

Comparatively little recent progress has been made in the theory of temperature effects on absolute index. It is considered, however, that this effect consists of at least two well-defined components which may, and often do, have opposite signs. The more frequently mentioned component is the direct result of thermally produced changes in density and its sign is always as indicated by the equation

$$\frac{\partial \bar{n}}{\partial t} = f(\bar{n}) \frac{dd}{dt} \tag{24}$$

where $f(\bar{n})$ is a positive function, which may be variously approximated (for example as $\bar{n}-1$, $\bar{n}^2-1$, $\frac{\bar{n}^2-1}{\bar{n}^2+2}$, etc.). Consequently, for media which expand when heated, this change in index is negative as temperature increases, and this effect of temperature is not a function of wave length but relates primarily to conditions for infinite wave length. As mentioned for air in part 1 of section II, the second component is ascribed to changes in the resonance frequencies of the media. The increase in volume which usually takes place with rising temperature is often accompanied by a capacity for absorbing radiation of longer wave length. Thus, under such circumstances, ultraviolet absorption bands are "shifted" toward the longer wave lengths of the visible region while the long wave lengths of infrared bands become still longer. Obviously, then, these absorption components of temperature coefficients of index are functions of wave length.

The velocity of propagation of radiation of a wave length longer than that corresponding to the effective absorbing frequency is decreased, while that of shorter wave length is increased. Consequently, for media whose principal effective absorption bands lie in the ultraviolet, this total absorption-band component of refractive index usually increases as temperature increases, while the reverse is true for media with predominant infrared absorption. In most optical glass the index change (in and near the visible spectral region) that is ascribable to the ultraviolet absorption bands predominates over the combined effects of the directly produced density change and the change caused by shifting of the infrared bands. For some crown glasses, however, the opposing tendencies are about equal in absolute value, and the index sensitivity to temperature is quite negligible. For a few crowns of very low index and somewhat unusual chemical composition the density and infrared effects predominate and negative temperature coefficients of absolute index are found, especially for the longer wave lengths of the visible spectrum.

(a) THERMAL COEFFICIENTS OF ABSOLUTE REFRACTIVE INDEX

For a few optical glasses temperature coefficients of absolute index are readily available through the work of C. Pulfrich [25] and of J. O. Reed.[26] Also, such coefficients can be readily computed from coeffi-

[25] Ann. Physik **45**, 609–665 (1892).
[26] Ann. Physik **65**, 707–744 (1898).

cients of relative index that have been determined by C. S. Hastings, [27] G. Müller, [28] H. Fizeau, [29] and J. W. Gifford; [30] or they may be estimated from the graphs published by C. G. Peters.[31] From a critical examination of these data, and also from unpublished results obtained in this laboratory, it is inferred that chemical composition is a predominantly important factor in determining this thermo-optical relationship for glass. Accordingly, it is difficult to make concise general statements, with a useful degree of precision, about the quantitative effects of temperature variations on the refractivity of glasses.

At usual room temperatures the values of $10^6 \times \triangle \bar{n}/\triangle t$, for the sodium-lines indices of flint glasses vary from approximately 0 for some light flints containing barium to +14 for those with highest lead content. For low-index glasses it is often considered that the temperature coefficients of absolute index are small and that they lie within a narrow range as compared with flint glasses. Available data confirm this view for the optical crowns in frequent use, the range in their coefficients being −1 to +3. Measurements in this laboratory show, however, that certain fluor crowns have values of −3 while for Pyrex and fused-quartz glasses of similar refractivity the coefficients are +5 and +9, respectively.

For crystals the range in refractive-index sensitivity to temperature is greater than for glasses. It is sufficient to mention sylvite, which, at room temperature, has a coefficient of approximately -34×10^{-6}, and calcite with its value of $+11 \times 10^{-6}$ for the extraordinary ray.

Numerous published data concerning the temperature coefficients of refractive index of liquids show that such values are all negative (direct density effect predominating over that of the absorption shift in the ultraviolet) and very much larger in numerical value than those for most solids.[32] It is useful to remember, however, that the percentage variations among such temperature coefficients for different liquids are, in general, relatively small compared with similar variations for solids. For a large number of transparent and semitransparent liquids (including numerous oils) the value of $\triangle \bar{n}/\triangle t$ is approximately expressed as -4×10^{-4}, although a number of organic liquids have values ranging from −4 to -6×10^{-4}. Water with a value of -1×10^{-4} is a most important exception and, on the other hand, there are some optically dense liquids which have unusually high (negative) temperature coefficients of index, such, for example, as −7 and -8×10^{-4} for methylene iodide and carbon disulphide, respectively.

(b) APPROXIMATE RANGE IN TEMPERATURE TOLERANCES FOR SOLIDS AND LIQUIDS

When considering temperature tolerances for general refractometry it must be remembered that one may have no prior knowledge of the media and their temperature coefficients of index. From the values given above it is evident that even for glasses known to be the usual crowns and light flints, the temperature of the sample during refrac-

[27] Am.J.Sci. [3] **15,** 269-275 (1878).
[28] Publicationen Astrophysikalischen Observatoriums Potsdam **4,** 149-216 (1885).
[29] Ann.chim.phys. [3] **66,** 429-482 (1862).
[30] Proc.Roy.Soc. (London) **A91,** 319-321 (1915); **A100,** 621-626 (1921-22).
[31] BS Sci.Pap. **20,** 635 (1926) S521.
[32] The absolute value of the ratio between temperature coefficients of liquids on the one hand and of glasses and common optical crystals on the other may be very roughly expressed as 100. Consequently, for liquids, coefficients of relative and of absolute refractive index are practically identical, whereas for glasses and crystals they frequently are quite different and may be of opposite sign.

tive-index determinations must be known within the limits of approximately $\pm$ 0.3° C to correspond to a limiting error of $\pm 1 \times 10^{-6}$ in index. For Pyrex glasses and for fused quartz the corresponding temperature tolerances are $\pm$ 0.2 and $\pm$ 0.1° C, respectively. Possibly, precision and accuracy in temperature measurement within approximately these limits can with care be obtained when a glass prism is mounted on a spectrometer table and exposed to the air of a room in which the temperature is constant or changes but slowly. When, however, the denser flint glasses are considered, it is found that the tolerances are reduced to $\pm$ 0.07° C (and even to $\pm$ 0.03° C for determinations with the shorter wave lengths of the visible spectrum).

Consequently, without considerable prior knowledge concerning a particular transparent solid, it is not advisable to attempt sixth-decimal-place refractometry unless temperature is controlled and measured to within $\pm$ 0.1° C or better. It is, therefore, highly desirable to provide a constant-temperature prism housing, even for work in a constant-temperature room, and to determine all indices with respect to a stirred air bath surrounding the prism.

Tolerances in temperature control and measurement during refractive-index determinations on liquids to within one unit of the sixth decimal place are so strict that there seems to be no published account of a serious attempt to reach such precision. The requirements are $\pm$ 0.01° C for water at room temperature, and approximately $\pm$ 0.002° C for liquids of average thermo-optical sensitivity.

2. EFFECTS OF PRESSURE ON REFRACTIVE MEDIA

L. Zehnder [33] found that water under pressure increases in absolute index by 15×10^{-6} per atmosphere at 20° C, and he favored the Gladstone and Dale relation, the constancy of $(n-1)/d$, when the density of liquids is varied by pressure. W. C. Röntgen and L. Zehnder [34] give data on similar increases in index for several other liquids. Although they do not choose between the Gladstone and Dale relation and that of Lorenz-Lorentz, their results are in general somewhat more favorable to the former.

F. Pockels [35] investigated the effects of unidirectional pressure on seven kinds of glass, using Neumann's equations for expressing the influence of elastic deformation on the propagation of light, and he found the Newton relation, $(n^2-1)/d$, somewhat more nearly constant than that of Gladstone and Dale or of Lorenz-Lorentz. L. H. Adams and E. D. Williamson [36] also have published results on the relation between birefringence and stress in various types of glass and have confirmed Pockels' results where comparisons can be made.

There is, however, a general lack of direct experimental evidence relating to the effect of atmospheric-pressure variations on the absolute refractivity of transparent media, and particularly so for optical glasses. Both Hovestadt [37] and Adams and Williamson have mentioned the conputation of such effects from Pockels' work and the equations of Neumann but, unfortunately, the necessary constants

[33] Ann. Physik [3] **34**, 91–121 (1888).
[34] Ann. Physik [3] **44**, 49–50 (1891).
[35] Ann. Physik [4] **7**, 745–771 (1902); also, for important corrections, see **9**, 221 (1902,) and **11**, 652 (1903).
[36] J. Wash. Acad. Sci. **9**, 609–623 (1919).
[37] H. Hovestadt, Jena Glass, appendix H, page 409 (Macmillan and Co., London, 1902).

characteristic of different media are known only for the seven glasses used by Pockels, and two [38] of these are unusual alumino-borates.

(a) VARIATIONS IN ATMOSPHERIC PRESSURE

Some indications concerning the effects of atmospheric-pressure changes on liquid and solid refractive media may, however, be obtained from a consideration of the index-density relationships together with the published data on β, the compressibility at constant temperature, and on its reciprocal, K, the "bulk modulus" or modulus of volume elasticity. If, in accord with Pockels' results for glass, the Newton form $(n^2-1)=C'd$ is written to express the index-density relation for a medium having a modulus $K=-V\,dP/dV$, and a density $d=m/V$, then

$$d\bar{n}=\frac{(n^2-1)}{2nK}dP \tag{25}$$

is obtained as the differential relation between refractive index and pressure. Or, if the index-density relation is $(n-1)=C''d$, one finds according to this Gladstone and Dale premise

$$d\bar{n}=\frac{(n-1)}{K}dP \tag{26}$$

as an alternative index-pressure relationship. Similarly, from the Lorenz-Lorentz expression

$$d\bar{n}=\frac{(n^2-1)(n^2+2)}{6nK}dP \tag{27}$$

would be written.

In view of the analysis which Pockels made from his experiments on glass under pressure, equation 25, rather than 26 or 27, is preferable for solids, while from the work of Zehnder and of Röntgen and Zehnder with pressure applied to liquids it may be inferred that equation 26 is more suitable for liquid media. The writer has found, however, that Pockels' data agree with an index-density relation

$$\left(\frac{n^2-1}{n^2+2}\right)^5=C'''d^3 \tag{28}$$

much more closely than with the Newton relation, and consequently the differential equation

$$d\bar{n}=\frac{(n^2-1)(n^2+2)}{10nK}dP \tag{29}$$

is preferable to equation 25. Since $K=E/[3(1-2\sigma)]$, where E is Young's modulus of elasticity and σ is Poisson's ratio, equation 29 may be written

$$d\bar{n}=\frac{3(1-2\sigma)(n^2-1)(n^2+2)}{10nE}dP \tag{30}$$

[38] The Pockels glass listed as 0.428, $n=1.5123$, was not, as originally supposed, an alumino-borate like his two other crown glasses but, according to subsequently published corrections (see footnote 35, p. 409), was a borosilicate glass. The revised data are free from peculiarities which marked the original exhibit. Nevertheless the errors continue to be propagated in the literature or, as in the International Critical Tables, 2, page 106, this important glass is omitted from consideration.

or, the change in index may be computed approximately from

$$\Delta\bar{n}=\frac{0.15(n^2-1)(n^2+2)}{nE}\Delta P \tag{31}$$

if the constant value $\sigma=0.25$ is used instead of experimentally determined values [39] which with few exceptions lie within the range from 0.21 to 0.27.

Equation 26 has been used in computing $\Delta\bar{n}$ for water, ethyl ether, ethyl alcohol, benzene, and carbon disulphide, using for $1/K$ averages of several published values for the compressibility of these liquids. The results agree within the limits of ± 10 percent with published experimental values. Equation 29, which is based on the new index-density relation, has been used in computing $\Delta\bar{n}$ for Pockels' glasses when subjected to changes in hydrostatic pressure, and the results lie within approximately ± 5 percent of those computed from the actual experimental constants in the manner suggested by Pockels. These 5 percent differences compare with 15 and 20 percent differences that are obtained when a similar computation is made by equation 25, which is based on the Newton index-density relation as favored by Pockels. If, however, the approximate form (equation 31) is used instead of equation 29 the differences are as large as 15 percent.

From equation 26 the tolerance in atmospheric- or other hydrostatic-pressure changes for work on liquid media is

$$T_{\Delta P}=\pm\frac{0.000001}{(n-1)\,\beta} \tag{32}$$

for a limiting error of $\pm 1\times10^{-6}$ in refractive index. For ethyl ether or carbon disulphide the limits ± 12 mm are found, and for ethyl alcohol or benzene they are ± 17 mm. Consequently, pressure corrections of this nature should not be entirely neglected. The less compressible liquids water and glycerin have the correspondingly more liberal tolerances of ± 47 and ± 72 mm, respectively, and they require corrections only for extremes of pressure variations or for reductions to standard conditions after measurements are made where the prevailing barometer level is appreciable different from 760 mm.

From equation 31 one may write

$$T_{\Delta P}=\pm\frac{0.000007nE}{(n^2-1)(n^2+2)} \tag{33}$$

as the tolerance in ΔP for sixth-decimal-place refractometry of glass. The values of E seem to range within ± 10 percent of the average 0.72×10^6 atmospheres for borosilicate glasses not containing lead oxide or phosphoric acid,[40] and except for a few extremes all other glasses seem to have values of E which lie within ± 10 percent of 0.58×10^6 atmospheres. Hence, considering only the absolute index of glass, it is evident that the tolerance in measurement or control of air pressures is seldom if ever [41] less than about 1/2 atmosphere, and therefore of no moment.

[39] R. Straubel, Ann. Physik [3] **68**, 409 (1899); or see page 193 of reference cited in footnote 37, page 409.
[40] See page 159 of reference cited in footnote 37, page 409.
[41] Glasses containing approximately 74 percent of PbO may perhaps be exceptions. See part b of this section.

In connection with the subject of pressure effects on absolute index it should be remembered, however, that corrections of this nature should be considered if one attempts a precise comparison between relative indices and those observed under actual vacuum conditions. In the case of liquids, it becomes imperative, even for accuracy in the fifth decimal place, to distinguish between values actually measured in a near vacuum (under their own vapor pressure) and those which are reduced from relative measurements by considering only the effect of pressure on the ambient air.

(b) STRESS AND BIREFRINGENCE

In addition to hydrostatic-pressure effects there should also be considered those effects which are due to unequally distributed stresses within media. Such stress distribution is caused, for example, by improper annealing of glass and by the improper mounting or tight clamping of optical components, especially under varying temperature conditions. The birefringence that is produced in this manner is commonly used as a measure of the internal stress and it seems desirable, if possible, to use birefringence as a measure of that change in refractive index which accompanies the stresses.[42]

From Pockels'[43] work it is possible to express the ratio between the change in index, Δn_y or Δn_z, and the absolute birefringence, $\Delta n_y - \Delta n_z$. For the ray which vibrates parallel to the axis of stress

$$\frac{\Delta n_y}{\Delta n_y - \Delta n_z} = \frac{2\sigma}{1+\sigma} - \frac{(1-2\sigma)\frac{q'}{v'}}{(1+\sigma)\left(\frac{p'}{v'} - \frac{q'}{v'}\right)} \tag{34}$$

and for the transverse ray

$$\frac{\Delta n_z}{\Delta n_y - \Delta n_z} = \frac{2\sigma}{1+\sigma} - 1 - \frac{(1-2\sigma)\frac{q'}{v'}}{(1+\sigma)\left(\frac{p'}{v'} - \frac{q'}{v'}\right)} \tag{35}$$

where p'/v' and q'/v' are experimentally determined constants for a given medium and σ is Poisson's ratio. For glass in the index range 1.5 to 1.75 the Pockels' data lead to higher absolute values for the transverse ray ratio, while for his glass of $n=1.96$, equation 34 gives the larger ratio. Consequently, it may be said that the tolerance in absolute stress-birefringence $\Delta n_b = (\Delta n_y - \Delta n_z)$, in millimicrons per centimeter, for sixth-decimal-place measurements of refractive index is at least as large as

$$T_{\Delta n_b} = \pm \frac{10}{f\left(\sigma, \frac{p'}{v'}, \frac{q'}{v'}\right)} \text{ millimicrons per cm} \tag{36}$$

[42] For clearness it may be necessary to mention that any piece of unannealed glass in which such stresses exist is a balanced system involving both tensions and compressions so that the index changes which are produced are of opposite sign and offset each other. (See L. H. Adams, J. Franklin Inst. **216**, 39–71 (1933).) Nevertheless, portions of the glass may show an average birefringence of a given sign and therefore experience a correspondingly changed index. Such limited portions of the medium should be individually considered because such a procedure corresponds closely to conditions under which optical-glass components are often measured and used, namely, at partial rather than at full apertures.

[43] Ann. Physik [4] **7**, 745–771 (1902); also for important corrections, see **9**, 221 (1902), and **11**, 652 (1903).

where the denominator is computed according to equation 35 for glasses of index $<1.8+$ and by equation 34 for glasses of index >1.9, approximately.

Equation 36 with each of these denominators written in turn, has been used in computing the corresponding values of this tolerance for the seven Pockels glasses, and figure 1 shows the chief results. It does not seem clear where the curves of this figure should cross [44] and accordingly they are not drawn in full. In any event, it is evident that stress-birefringence differs greatly in the degree of sensitivity with which it can serve to measure the variations in index which may

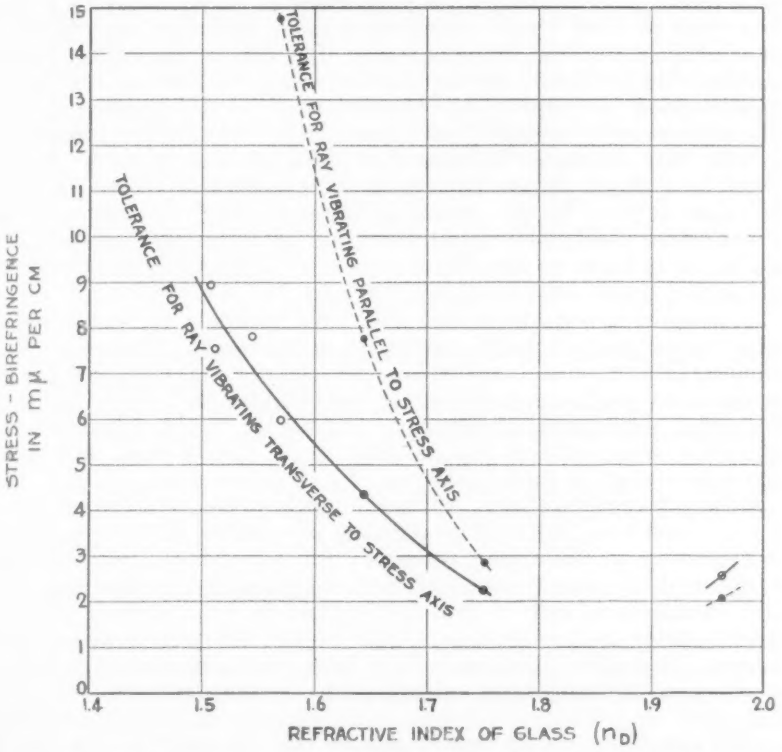


FIGURE 1.—*Tolerances in stress-birefringence for optical glass on which refractive index is measured to* $\pm 1 \times 10^{-6}$.

Where the orientation is indefinite, the safer tolerance is obviously that indicated by the lower curve.

exist because of the stresses in various kinds of glass. For flints it is obvious that the birefringence present should be much lower than for crowns, and consequently the annealing requirements and schedules for flints should not be too readily neglected because of the comparative ease with which their stress-birefringence seems to be reduced. Nevertheless, remembering the Rayleigh limit of one-quarter wave

[44] Pockels concludes that p' must equal q' for some glass containing about 74 percent of PbO (index 1.8+) and consequently from equations 34, 35, and 36 it seems that for p' and q' not zero the crossing of the curves of figure 1 should occur at zero tolerance (at least for all values of σ other than 0.5, which is the limiting value for the case of an incompressible medium). On the other hand, for $\sigma=0.5$ when $p'=q'$, or whenever $p'=q'=0$, the ordinate of the point of crossing appears indeterminate as judged from these equations.

length of permissible phase difference and the resulting requirement [45] that optical glass be uniform in index within ± 0.000007 per cm, it seems that tolerance limits of from 5 to 10 mμ birefringence per cm are of a proper order of magnitude for most of the requirements of optical glasses.

3. HEAT TREATMENT, CHEMICAL HETEROGENEITY, AND STRIATION OF GLASS

When a piece of glass has been annealed in such manner that the stress-birefringence is within the tolerances shown in figure 1 it is very likely that it is also homogeneous in physico-chemical sense. The work of Tool [46] and others has shown, however, that there is a possibility of residual inhomogeneity that can be caused by furnace-temperature gradients during the annealing and which may not be accompanied by appreciable birefringence in the finished product. The sensitivity of optical glass to variations in annealing temperature is such that decreases in refractive index of from 2 to 6×10^{-5} are found in various glasses at ordinary temperatures corresponding to increases of 1° C in the annealing temperature.[47] These annealing-temperature coefficients of index of glass are in general approximately ten times as large as the ordinary temperature coefficients of refractive index, which were considered in part 1 of this section.

In measuring refractivities to five or six decimals, and when making intercomparisons of such results, it is necessary, therefore, before drawing inferences and conclusions, to consider the possibility of small temperature gradients in the annealing furnaces and also to remember the great difficulties of securing sufficiently exact duplications of annealing temperatures and cooling rates during runs in different furnaces or even in successive runs of a given furnace.

Before the optical effects of nonuniform heat treatment were known, it was considered difficult or perhaps impossible to secure chemical homogeneity to the extent necessary for refractive-index uniformity to the sixth or even to the fifth decimal place, even when concerned with distances of only a few centimeters in good optical glass. A careful study and analysis of Fritz Eckert's [48] investigation shows, however, that after "fine annealings" the maximum spread chargeable to chemical heterogeneity within each of three melts of a barium flint glass was $\pm 1\times10^{-5}$ or less in refractive index. Also, a report on careful annealings of six lens blanks at this Bureau [49] shows that the chemical heterogeneity, if any, was confined entirely to a few units of the sixth decimal place of refractive index.

Such gross and intensely localized heterogeneities as striae do not occur to any large extent in the best optical glass, but it is sometimes desirable to extend minimum-deviation measurements to less perfect glasses. Consequently, it would be of interest to know the extent to which striation can be present without seriously affecting index measurements. Unfortunately little definite information is available.

Striae commonly exist in two well-known forms—as "cords" or "veins" and as sheet striae or "ream." Their optical properties are,

[45] See page 720 of BS Sci.Pap. **22**, (1928) S572.
[46] A. Q. Tool and C. G. Eichlin. J.Opt.Soc.Am. **4**, 359 (1920); BS J.Research **6**, 525 (1931) RP292.
[47] A. Q. Tool, L. W. Tilton, and E. E. Hill, J.Optical Soc.Am. and Rev.Sci.Inst. **12**, 490–491 (1926). L. W. Tilton, J.Wash.Acad.Sci. **20**, 12–13 (1930). See also Annual Report of the Director of the Bureau of Standards, U. S. Department of Commerce, pages 11, 23, 21, and 25, of years 1925, 1927, 1928, and 1929, respectively.
[48] Z.tech.Physik **7**, 282–287 (1926).
[49] L. W. Tilton, A. N. Finn, and A. Q. Tool, BS Sci.Pap. **22**, 719 (1928) S572.

of course, different from those of the adjacent media, and apparently there is a rather abrupt transition [50] at the interfaces. According to prevailing ideas [51] it may perhaps be assumed that in general the principal and only important effect is a scattering of light, which results in loss of contrast and consequent poor definition of the image of the collimator slit. This is probably true if the striae are present mainly as cords and if they do have abrupt boundaries.

On the other hand, when the striae consist of well-stratified layers or extensive sheets of "ream" the conditions are quite different. Unless the planes of stratification are approximately parallel to the light paths, all of the rays traverse striae and suffer a consequent acceleration or retardation, but it is usually found that an image of the slit is fairly well outlined even when one uses prisms in which such striae are very numerous. If the striae are so thin, or the difference in refractive index so small that beams emerging from adjacent kinds of glass differ in phase by less than one-quarter wave length, then the measured deviation produced by such a composite prism corresponds to that for a similar prism having a fictitious index, n_3, intermediate in value between n_1 and n_2, indices of the "normal" glass and the striae, respectively. In fact, if s is the proportion by volume of the striae present, one may write

$$n_3 = n_1 + s(n_2 - n_1) \tag{37}$$

as an estimated condition which seems probable for the case of a quasi regular composite prism of this type.

Since striae may differ in index from the normal glass by 3×10^{-4} (an average of some values which were observed by Smith, Bennett, and Merritt) it seems that the presence of certain types of striae in amounts exceeding 0.3 percent of the whole volume of glass should be considered a potential source of errors that may appreciably affect the sixth decimal place of refractive-index determinations.

IV. REQUISITE PRECISION IN SOURCE OF RADIATION

It is desirable to know to what extent doublets and complex lines may be used in sixth-decimal-place refractometry, and to decide whether or not it is necessary to specify the conditions under which a source of radiation is operated. For such purposes it is sufficient quantitatively to consider the dispersion in relative index for a few highly dispersive substances.

If the simple Cauchy dispersion formula

$$n - 1 = a + \frac{b}{\lambda^2} \tag{38}$$

is written to approximate (with two constants) the result of experiments over a limited spectral interval it is evident that

$$\frac{dn}{d\lambda} = -\frac{2b}{\lambda^3} \tag{39}$$

[50] A. A. Michelson, BS Sci.Pap. **15**, 41 (1919) S333.
[51] T. T. Smith, A. H. Bennett, and G. E. Merritt, BS Sci.Pap. **16**, 75 (1920) S373. A. Arnulf, Rev. optique **6**, 6-20 (1927).

can be written to show how refractive index varies with wave length within the specified interval. Consequently, one may consider

$$T_{\Delta\lambda}=\pm\frac{5\lambda^3}{b\times10^7} \tag{40}$$

as a suitable tolerance in wave length of source for a limiting error of $\pm1\times10^{-6}$ in index.

For use with wave lengths measured in angstroms the constant b is seldom as large as $+25$ or $+30\times10^5$ (values for carbon disulphide and densest flint glass of index $n_D=1.92$, respectively, computed for the shortest wave-length region of the visible spectrum) and thus any uncertainty or variation in the source of less than ±0.01 angstroms is not of consequence for wave lengths longer than approximately 4000 A. For the great majority of substances on which refractive indices are precisely determined, the tolerance is appreciably more liberal. Water and fluorite, for example, have the corresponding minimum or safe tolerances of ±0.10 and ±0.13 A, respectively.

V. PRECISION AND ACCURACY ATTAINABLE IN MINIMUM-DEVIATION REFRACTOMETRY

In this and in previous papers [52] many of the difficulties of precise prism refractometry, particularly by the minimum-deviation method, have been discussed. The number, N, of sources of error is fairly large. At least nineteen of them have been quantitatively discussed in these investigations and the discussions are briefly summarized in table 5. Several of the errors, say $(N-N_1)$ of them, are easily held within limits which are small compared with $\pm1\times10^{-6}$ in index. In no respect is it found impossible, and in few if any instances does it seem unreasonably difficult to control or correct within that tolerance limit. With the exception of error arising from incorrect prism orientation, practically all contributions to the final error in index are equally likely to have positive or negative signs in any extensive and well-arranged observational program. Consequently the algebraic sum is never large.

If, as an approximation to the worst case, N_1 of the contributed errors are large compared with the rest and are all about equal in absolute value, say 1×10^{-6}, then the probable error in the final index is $\sqrt{N_1}\times10^{-6}$. For several years the individual tolerances corresponding to $\pm1\times10^{-6}$ have been used in this refractometric laboratory and it seems that probable errors in refractive indices precisely determined by the minimum-deviation method seldom exceed ±2 or 3×10^{-6}. Hence the existence of some five or ten fairly important sources of accidental error is inferred. Whenever less precision is obtained after the expenditures of reasonable effort in the use of fairly good equipment, the difficulty is probably to be sought not in any one or two particularly important sources of error but in a combination of several matters which have been overlooked or deliberately neglected as inconsequential.

[52] See references listed in table 5.

TABLE 5.—*Summary of sources of refractive-index error that have been quantitatively discussed*

TABLE 5.—*Summary of sources of refractive-index error that have been quantitatively discussed*

References to BS J. Research			Quantity evaluated or controlled			±Tolerances for various refractivities of sample ($\Delta n = \pm 1 \times 10^{-6}$, $A = 60°$)				
Volume	Page	Formula	Name	Symbol	Unit	$n = 1.3$	$n = 1.5$	$n = 1.7$	$n = 1.9$	Provisory remarks [1]
1929										
2	921	8	Prism angle	ΔA	Second of arc	0.57	0.33	0.22	0.16	
2	921	9	Double deviation	$\Delta 2D$	do	0.56	0.62	0.80	1.5	
1931										
6	72	14	Prism orientation	$P.E.i$	Minute of arc	3.9	3.1	2.7	2.4	(Index error always +).
1933										
11	41	23	Prism surface sagitta	s'	Wave length	0.27	0.14	0.08	0.04	1 cm diam. of surface area.
11	42	24	Prism translation	$P.E.\epsilon_0$	Millimeter	1.3	0.7	0.4	0.2	$s' = 0.02\lambda$.
11	47	33	Eccentricity of prism-table axis.	ϵ	do	0.3	(Very large)	0.2	0.1	s' = tabulated values.
11	52	45	Collimator focusing	ΔF_C	do	2.9	2.0	1.8	2.7	$f_o = 400$ mm, $\epsilon = 0.2$ mm.
1934										
13	117	------	Air composition	------	Proportion by volume.	(Relatively large tolerances—see reference cited)				CO_2-free dry air.
1935										
14	400	10	Air temperature	Δt_a	Degree C	0.77°	0.67°	0.59°	0.53°	$t = 0°$ C.
14	400	12	Air pressure	Δp_a	Millimeter of Hg.	2.2	1.9	1.6	1.5	
14	401	16	Air humidity	Δv	do	15.	13.	12.	11.	
14	403	21	Abnormal CO_2 in air	Δc	Proportion by volume.	0.005	0.004	0.004	0.003	
14	408	------	Temperature of certain glasses	------	Degree C	------	Soda lime 0.3°; Fused quartz 0.1°	Dense flint 0.2°	Densest flint 0.07°	$\lambda = 5893$ A.
14	408	------	Temperature of certain liquids.	------	do	Water 0.01°	Many oils 0.002°	CS_2 0.001°	------	$\lambda = 5893$ A.
14	411	32	Hydrostatic pressure on glass	ΔP	Atmosphere	------	0.5	0.5	0.5	
14	411	33	Hydrostatic pressure on certain liquids.	ΔP	Millimeter of Hg.	Water 47.; Ether 12.	Glycerin 72.; Benzene 17.	CS_2 12.	------	
14	412	36	Stress-birefringence in glass	Δn_b	$m\mu$/cm	------	9.	3.	2.	(? at $n = 1.8+$).
14	415	37	Striae in glass	s	Proportion by volume.	0.003	0.003	0.003	0.003	$n_2 - n_1 = 0.0003$.
14	416	40	Wave length of light source	$\Delta\lambda$	Angstrom	Water 0.10	Fluorite 0.13	CS_2 0.014	Densest flint 0.010	$\lambda = 4000$ A.

[1] For explanations and for other pertinent limitations and conditions, see discussions given in references cited in columns 1 to 3.

It is a much more difficult matter to state precisely what accuracy is attainable. Tests of the accuracy of angle measurement by the use of a prism polished on all three faces are of fundamental importance. Torsion and mechanical strains in the goniometer constitute a particularly dangerous source of systematic error which is seldom entirely constant and cannot always be effectively eliminated. Fortunately, those errors which would be systematic if neglected are automatically replaced by residual accidental errors when proper corrections can be and are applied. In this laboratory no reason has been found for suspecting that residual systematic errors in precise index measurement with a spectrometer are materially in excess of the precision which is attained.

WASHINGTON, January 26, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP777

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

EFFECT OF GRANULOMETRIC COMPOSITION OF CEMENT ON THE PROPERTIES OF PASTES, MORTARS, AND CONCRETES

By J. Arthur Swenson, Lacey A. Wagner, and George L. Pigman

ABSTRACT

Data obtained in studies of five laboratory-ground clinkers and one commercial cement are presented. Each of the ground clinkers was separated into the following five nominally sized fractions: 0 to 7, 7 to 22, 22 to 35, 35 to 55, and >55 microns. The commercial cement was separated into only four fractions, no separation being made of the material coarser than 35 microns. Tests were made on the individual fractions as well as on four cements prepared by blending the fractions in various proportions. The specific surfaces of these blended cements ranged from 1,350 to 3,300 cm^2/g. It was found that the 0–7 micron material is very valuable because of the plastic qualities which it confers upon the concrete mixes and also because of the high contribution which it makes to the early strength. The other four fractions were found lacking in plasticity and the ability to hold water, and the rate of strength development decreased with increasing grain size. The contribution of the 0–7 micron fraction to the strengths of the blended cements was calculated by an algebraic method based on the assumption that the contribution of any fraction to the strength of a blended cement is equal to the product of the decimal part of the blend composed of that fraction and the strength of the fraction when tested by itself. The values thus calculated were found to be of the order which might be expected. The analysis of all the strength data tended to prove that the compressive strength of concrete is very nearly a direct function of the amount of cement which has reacted with water. When the strengths were plotted against specific surface, one line was obtained for the blended cements and another line for the individual fractions. When these same strengths were plotted against quantities which should at least be approximations of the amount of hydrous material, all of them fell on one line.

CONTENTS

	Page
I. Introduction	420
II. Preparation and character of fractions and blended cements	421
1. Fractions	421
(a) Description of elutriation stacks	421
(b) Method of separating	422
(c) Character of fractions	422
(d) Chemical compositions of fractions	424
(e) Addition of gypsum to fractions	425
2. Blends of fractions	425
(a) Proportions and specific surfaces	425
(b) Method of preparation	426
III. Description of tests	426

	Page
IV. General notes on properties other than strength	427
1. Consistency and working qualities	427
(a) Fractions	427
(b) Blends of fractions	429
2. Time of setting	430
3. Soundness	431
V. Discussion of strength data	431
1. Introductory and general discussion	431
2. Theoretical considerations	436
3. Practical conclusions	446
VI. Summary	447

I. INTRODUCTION

The importance of knowing the relation between the particle-size distribution of cement and the properties of concrete has become more and more apparent during recent years. The study of high-early-strength cements has shown that the fineness of grinding greatly affects the rate of increase in strength. The development of plant equipment, such as finishing mills with air separators in closed circuit, making it possible to control the grinding much more closely and economically, has made the problem even more pertinent.

A considerable amount of work has already been done on the problem in other laboratories, both in this country and in Europe. An active controversy on the subject has been carried on in German technical publications during the past three or four years. Some of those who have contributed are Hans Kühl,[1] D. Steiner,[2] W. Weisgerber,[3] Hägermann,[4] E. Rissel,[5] A. B. Helbig,[6] and A. Eiger.[7] The problem has also been studied in France and Sweden.[8] In this country, the Portland Cement Association is at the present time carrying out an investigation of the subject at its Chicago laboratories.[9] S. Rordam, of the Cowham System Mills, has also published results of an investigation which he carried out.[10] Nevertheless, there still remains much to be done upon this problem, and the investigation described herein was undertaken with the hope of clearing up some of the controversial issues.

In this report the results obtained in studies of five different laboratory-ground clinkers and one commercially ground cement are presented. The clinkers were ground in laboratory mills without any gypsum being added. One of these clinkers (no. 5) was of the high-early-strength variety; the other four (nos. 1 to 4) were ordinary portland-cement clinkers. The commercial cement (no. 6) was a double-burned nonstaining brand of foreign manufacture.

After the clinkers had been ground to the desired degree of fineness and dried at a temperature of 110° C, they were separated into five size fractions by means of air elutriation. The nominal size ranges of the fractions were 0 to 7, 7 to 22, 22 to 35, 35 to 55, and 55 microns to the maximum size passing a no. 50 sieve. For the sake of brevity,

[1] H. Kühl, Zement **19,** 604, 630 (1930); Tonind.Ztg. **55,** 674 (1931); Zement **20,** 169 (1931).
[2] D. Steiner, Tonind.Ztg. **55,** 672 (1931).
[3] W. Weisgerber, Tonind.Ztg. **55,** 933, 946 (1931).
[4] Hägermann, Tonind.Ztg. **55,** 1099 (1931).
[5] E. Rissel, Zement **19,** 1079 (1930).
[6] A. B. Helbig, Zement **20,** 75 (1931).
[7] A. Eiger, Tonind.Ztg. **56,** 532, 558 (1932).
[8] O. Raulin, Ciment **35,** 342 (1930).
V. Bahrner, Tek.Tidsk. **59,** 114 (1929).
[9] Report of Conservation Bureau and Research Laboratory, Portland Cement Association, Spring Meeting of 1932.
[10] S. Rordam, Rock Products, p. 22 (July 30, 1932).

the designations 0–7, 7–22, 22–35, 35–55, and >55 will be used throughout this paper except in those cases where it may be advantageous to insert the word "micron." The foreign cement was so finely ground as delivered that it was possible to obtain only one sufficiently large fraction of material greater than 35 microns. This cement, accordingly, was separated into the four nominally sized fractions, 0–7, 7–22, 22–35, and >35 microns.

Studies were made of neat pastes, mortars, and concretes using each of the fractions individually as well as four blended cements prepared from the fractions. The fractions of the four ground portland cement clinkers and those of the commercial cement were tested without the addition of gypsum and also after 3.6 percent of gypsum had been added. Those of the high-early-strength clinker could not be tested without gypsum because of the quick initial set. It was found that 3.6 percent of gypsum was sufficient to retard the set of all but the 0–7 fraction of this clinker; the 0–7 fraction required 10 percent. The blends of the four portland-cement clinkers were tested, like the fractions, with and also without the addition of 3.6 percent of gypsum. Those of the high-early-strength clinker and the commercial cement were tested only after gypsum had been added, 3.6 percent in all cases except that of the finest blend of the clinker, to which 6.5 percent had to be added.

Throughout the remainder of this report the laboratory-ground clinkers will be referred to as cements, except when the context makes the use of the word "clinker" more desirable.

II. PREPARATION AND CHARACTER OF FRACTIONS AND BLENDED CEMENTS

1. FRACTIONS

(a) DESCRIPTION OF ELUTRIATION STACKS

The fractions were prepared in three air-elutriation stacks. The separations at 7 and 22 microns were made in the two stacks shown in figure 1. These two stacks operate in parallel, one blower supplying the air, which first enters the bottoms of the stacks, then passes upwards to the lead-off pipes connected to the dust collectors where it is forced through canton-flannel filtering bags before returning again to the blower. In the return lines, between the dust collectors and the blower, there are changeable orifices by means of which, together with differential pressure gages, the volume of circulating air, and hence the velocity of the air in the stacks, is controlled. A portion of the air from the blower is constantly by-passed through a refrigeration unit where it is cooled down to about 23° F. Upon returning to the blower the temperature of this air is raised to about 90° F. This process reduces the relative humidity to about 10 percent. Since the whole system is closed and there is no opportunity for the air to escape, the humidity of the circulating air is always kept very low. The stack in which the 35- and 55-micron separations were made is not shown in the figure, but it is of essentially the same design. The two stacks shown in the figure are 22 inches in diameter and have 6-foot straight sections with 4-foot cones. The third stack is 11 inches in diameter and has a 7-foot straight section with a 2-foot cone.

(b) METHOD OF SEPARATING

In making the separations the material was first blown in the two large stacks until most of the particles less than 7 microns in diameter had been removed. The next step consisted in blowing the residue, which was nearly all greater than 7 microns, in the same stacks at such a velocity as to effect a separation of a 7–22 fraction, which was caught in the filter bags. The residue was then blown in the 11-inch stack so as to yield a 22–35 fraction, which in turn was collected in the filter bag. After removal of the 22–35 fraction, the 35–55 fraction was blown off and collected. The residue from the last separation was sieved on a no. 50 screen, the material passing being designated as the >55 fraction. Each of the fractions was separately put through the stacks again and reblown at the lower size limit until shown by microscopic examination to be free from undersized material. It was found necessary to do this because the fractions as caught in the filter bags always contained a considerable amount of undersized material, caused by abrasion of the particles in the lower part of the cones. By this reblowing process a clean fraction was always obtainable as a residue from the lower outlets of the cones.

(c) CHARACTER OF FRACTIONS

Photomicrographs of typical fractions are shown in figures 2 and 3. Size-distribution curves for the fractions of three of the cements were obtained by means of microscopical measurements and counts. The fractions were mounted on microscope slides in an oil having a refractive index of 1.55.[11] The particle images were projected on a screen and measured with a calibrated rule. All the particles in a definitely bounded area in the middle portion of the field were measured and counted. In making the measurements an attempt was made to arrive at the average visible diameter of each particle; the "diameter" taken for an elongated particle was the mean of the longest and shortest visible dimensions. Different magnifications were used for different sized fractions; the finest fraction was magnified 5,700 times and the largest sized fraction 625 times. The weight-size distribution curves for the fractions of cement no. 4 are presented in figure 4. Those for the other two cements were quite similar. The size designations 0–7, 7–22, 22–35, 35–55, and >55 microns were arbitrarily chosen. It is seen in the figure that any two successive fractions overlap considerably.

The total surface area contained in unit weight of material, or what is commonly called the "specific surface", was calculated for each of the fractions from the data used in plotting the distribution curves. The relation between specific surface and distribution is given by the equation

$$ss = \frac{\Sigma nd^2}{\Sigma nd^3} 19050,$$

where ss is the specific surface in cm^2 per gram, n is the number of particles of diameter d microns, and 19050 is the surface in cm^2 of one gram of particles of diameter 1 micron and density of 3.15. The

[11] For a discussion of the effect of the refractive index of mounting medium, see *A sedimentation method for the determination of the particle size of finely divided materials (such as hydrated lime)*, by Dana L. Bishop, BS J. Research **12**, 173 (1934) RP642.

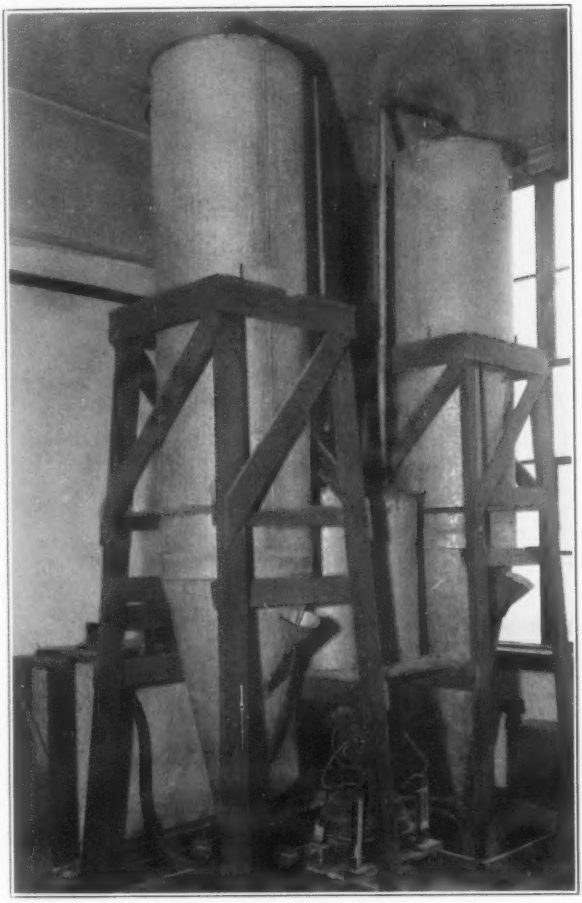


FIGURE 1.—*Air elutriation stacks.*

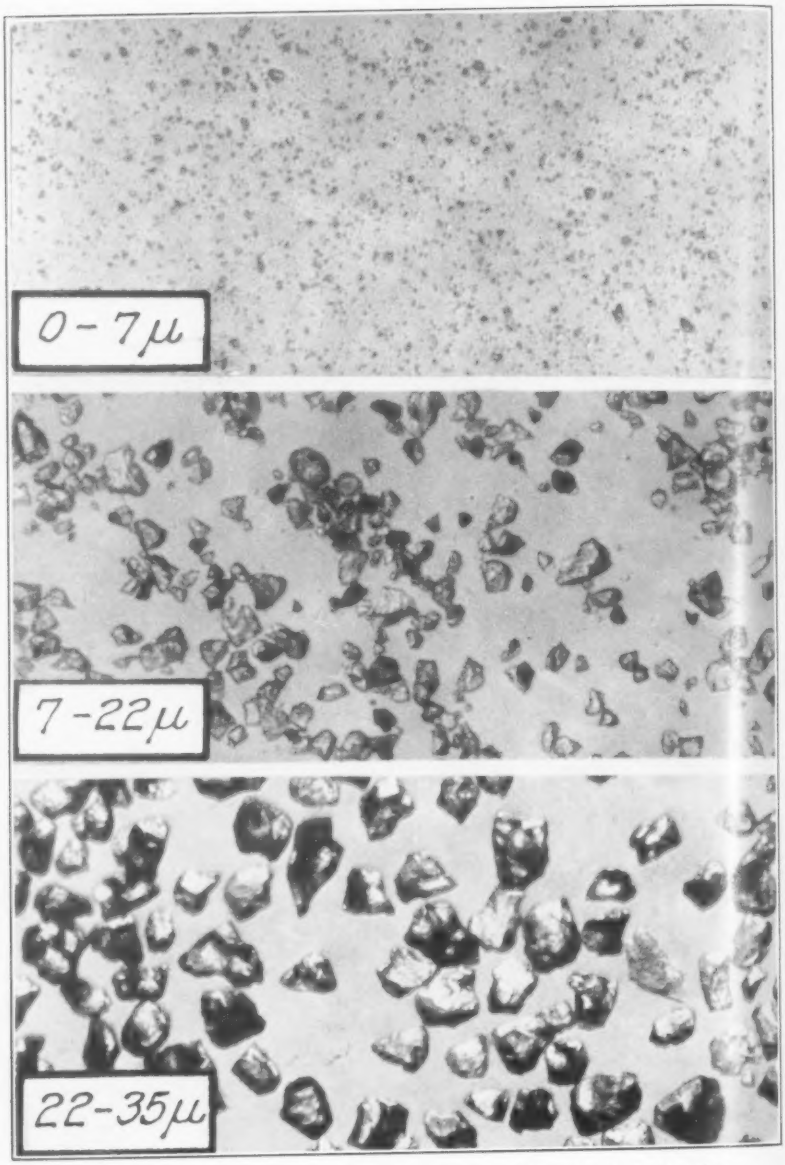


FIGURE 2.—*Photomicrographs of the 0–7, 7–22, and 22–35 fractions.*
(Magnification × 260.)

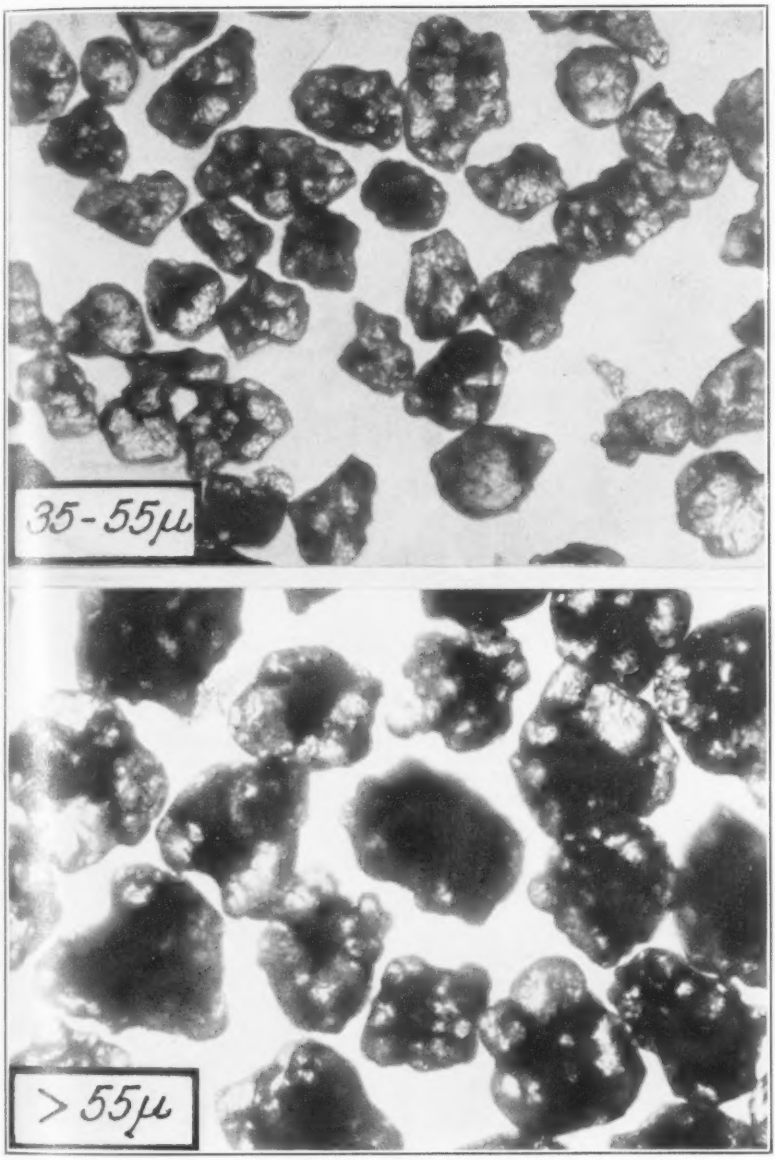


FIGURE 3.—*Photomicrographs of the 35–55 and >55 fractions.*
(Magnification × 260).

UNIV OF MICH.

specific surfaces obtained by this method for the fractions of cements 1, 3, and 4 are given in table 1 (A). Each of the values given is the average of the values obtained by calculation from measurements of 100 or more particles from each of two slides.

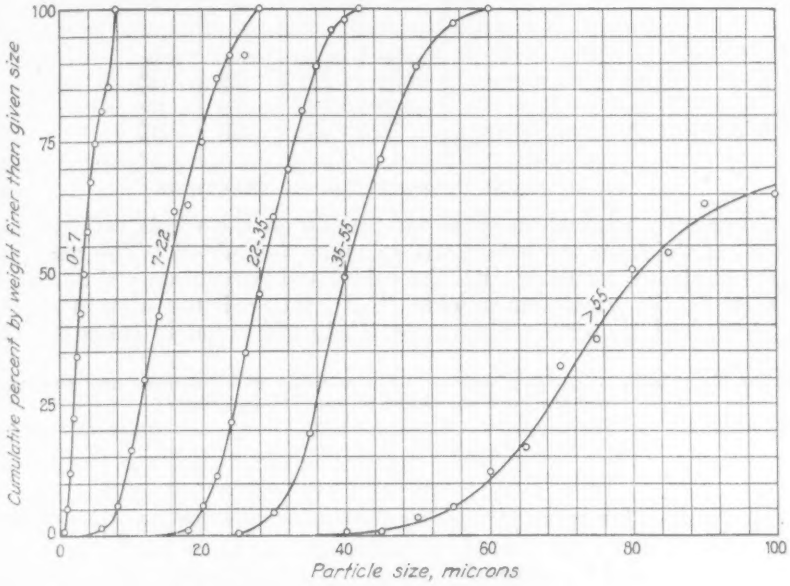


FIGURE 4.—*Size distribution of fractions.*

TABLE 1.—*Specific surface data*

(A) Specific surface of fractions as determined from microscopical counts:

Cement no.	Specific surfaces of fractions				
	0–7μ	7–22μ	22–35μ	35–55μ	>55μ
	cm^2/g	cm^2/g	cm^2/g	cm^2/g	cm^2/g
1	6600	1470	800	440	240
3	5000	1280	640	380	170
4	6380	1300	680	440	225
Average	6000	1350	710	420	210

(B) Proportion of each fraction in blends and specific surfaces of blended cements:

Blend	Percentage by weight, of fractions					Specific surface [1]
	0–7μ	7–22μ	22–35μ	35–55μ	>55μ	
						cm^2/g
F	20	20	20	20	20	1750
G	30	32	25	10	3	2450
H	47	24	20	7	2	3300
I	12	23	20	13	32	1300

[1] Calculated from average microscopical values for fractions of cements 1, 3, and 4.

TABLE 1.—*Specific surface data*—Continued

(C) Specific sufaces as determined by Wagner turbidimeter:

Cement no.	Specific surface of blend			
	F	G	H	I
	cm²/g	cm²/g	cm²/g	cm²/g
1	1690	2490	2960	1240
2	1740	2470	3190	1360
3	1620	2250	2950	1270
4	1720	2610	3050	1280
5	----------	2240	2945	1130

(d) CHEMICAL COMPOSITIONS OF FRACTIONS

Complete chemical analyses were made on the whole cements and on all of the fractions before any gypsum was added. The results of these analyses, together with the calculated percentages of dicalcium silicate (C_2S), tricalcium silicate (C_3S), tetracalcium alumino-ferrite (C_4AF), and tricalcium aluminate (C_3A) are given in table 2. The

TABLE 2.—*Chemical compositions of whole cements and fractions and compound compositions calculated on ignition-loss basis*

Cement no.	Fraction	Loss on ignition	SiO_2	CaO	Fe_2O_3	Al_2O_3	C_3S	C_2S	C_4AF	C_3A
	Microns	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Whole	2.4	21.0	65.5	3.7	6.9	56	19	11	12
	0– 7	6.4	20.3	65.3	3.6	7.3	59	14	11	13
	7–22	2.5	20.4	65.8	3.5	7.1	62	11	11	13
	22–35	1.5	21.2	65.5	3.6	7.2	52	22	11	13
	35–55	1.1	21.1	64.8	3.7	7.4	49	24	11	13
	>55	0.9	21.1	64.4	3.7	7.5	47	25	11	14
2	Whole	1.3	22.0	66.2	2.5	6.6	54	23	8	13
	0– 7	2.8	22.0	66.2	2.1	6.4	57	20	6	13
	7–22	1.2	22.3	66.5	2.2	6.5	54	23	7	14
	22–35	0.7	22.2	66.0	2.6	6.0	56	22	8	12
	35–55	0.6	21.6	65.6	3.0	6.7	54	22	9	13
	>55	0.7	21.2	65.2	3.5	6.9	53	22	11	12
3	Whole	1.4	21.0	65.5	2.3	7.1	56	18	7	15
	0– 7	4.1	20.7	65.6	2.3	6.7	62	13	7	14
	7–22	1.5	21.0	66.0	2.2	6.3	64	12	7	13
	22–35	0.8	21.6	65.5	2.3	6.6	56	20	7	14
	35–55	0.6	21.6	65.1	2.4	7.1	49	25	7	15
	>55	0.5	21.9	64.5	2.5	7.0	46	28	8	14
4	Whole	0.7	23.8	65.4	5.6	3.5	55	27	17	1
	0– 7	2.6	21.0	65.7	7.1	4.2	64	13	20	[a]1
	7–22	0.8	23.0	66.3	5.4	3.5	64	18	16	0
	22–35	0.5	24.7	65.6	5.0	3.4	51	33	15	1
	35–55	0.4	24.8	65.2	5.4	3.3	46	37	16	0
	>55	0.3	25.0	65.4	5.8	3.7	43	39	18	0
5	Whole	1.2	19.6	66.4	2.5	6.9	72	2	8	14
	0– 7	2.2	19.3	65.9	2.5	6.8	72	1	8	14
	7–22	0.7	20.4	66.7	2.4	6.7	67	8	7	14
	22–35	0.7	20.1	66.9	2.4	6.8	70	5	7	14
	35–55	0.6	19.4	66.8	2.5	7.3	72	1	8	15
	>55	0.3	19.5	66.5	2.6	7.4	70	3	8	15
6 [b]	Whole	4.8	21.1	69.4	0.5	1.7	63	14	1	4
	0– 7	9.5	16.3	70.0	0.4	1.0	49	10	1	2
	7–22	5.2	20.3	70.7	0.5	1.0	76	1	1	2
	22–35	2.2	23.8	70.1	0.6	1.3	76	11	2	2
	>35	1.5	25.5	66.8	0.6	2.0	51	35	2	4

[a] $2CaO.Fe_2O_3$.

[b] It is quite probable that cement no. 6 was partially hydrated and there is therefore some doubt as to its compound composition. The amounts of "free lime" present were determined by the ammonium-acetate method, which yields both $Ca(OH)_2$ and CaO, and were found for the whole cement and the fractions as given above to be as follows: 11, 24, 12, 4, and 1. In calculating the compound compositions given in the table the free lime was assumed to be all CaO although it possibly consisted largely of $Ca(OH)_2$. Since there is no way of knowing the exact source of the so-called free lime in a partially hydrated cement, the compound composition cannot be calculated with certainty. If the C_3S and C_2S in the "whole" fraction are calculated for the condition before the partial hydration (i. e., assuming no uncombined CaO) it is found that there were present of 80.0 percent of C_3S, 0.0 of C_2S, and 7 of uncombined CaO.

data on the five ground clinkers have been previously discussed in a paper entitled *Chemical analyses of the particles of various sizes of ground cement*, by E. T. Carlson and P. H. Bates,[12] published in the Oct. 22, 1932 issue of Rock Products.

As was brought out in this previous paper, the data show that there is a considerable amount of variation between the different fractions of any one cement as to chemical composition and potential compound composition. The finer fractions are in all cases higher in ignition loss than the coarser ones. The tricalcium silicate shows a tendency to be more concentrated in the finer, and the dicalcium silicate in the coarser fractions. The tricalcium aluminate and the tetracalcium alumino-ferrite seem to be about equally distributed between the fine and coarse particles.

The nonstaining cement, no. 6, which had not been analyzed at the time that the first paper was published, differs from the others in that it contains a very high percentage of "free" lime. The fact that most of this so-called "free" lime is found in the 0–7 fraction tends to indicate that this lime actually occurred largely in the hydrated form.[13] In other respects the cement exhibits the same general tendencies as the clinkers. When allowance is made in the case of the 0–7 fraction for the large portion of the lime which was not contained in the four usual constituents, the difference in tricalcium silicate between this fraction and the next two is very considerably reduced.

(e) ADDITION OF GYPSUM TO FRACTIONS

In adding the gypsum to the 0–7 fraction, the total required amount was first mixed with one kilogram of cement for one-half hour in a small mill containing a charge of stone pebbles. This mixture was then transferred to a larger mill, the remainder of the cement and a few wooden balls were added, and the mill was rotated for one-half hour. In the cases of the other four fractions the required amount of gypsum was added directly to the total amount of cement and the whole mixed with wooden balls for one-half hour. The gypsum used in this investigation was ground so as to be about 50 percent finer than 4 microns and 90 percent finer than 8 microns.

2. BLENDS OF FRACTIONS

(a) PROPORTIONS AND SPECIFIC SURFACES

The proportions of the fractions and the specific surface data for the blended cements prepared from the fractions, for cements 1 to 5 inclusive, are presented in table 1 (B) and (C). The specific surfaces were determined by direct calculation from the microscopical values for the fractions and also by means of the Wagner turbidimeter.[14] The weight and surface distributions are shown graphically in figure 5.

In preparing the four blends of cement no. 6, a total percentage of >35-micron material, which was equal to the sum of the percentages of the two largest sized fractions in the corresponding blends of the other cements, was used. Since this >35-micron material of cement no. 6 consisted mostly of material finer than 55 microns, its substitution for the >55 fraction as contained in the blends of the other

[12] The data are the same except that in the previous paper the constituents were presented as calculated on the no ignition-loss basis. In order to more accurately define the actual sizes, the nominal sizes 22–35, 35–55, and >55 have been adopted instead of 22–45, 45–75, and >75, respectively, for the largest sized fractions.

[13] Each of the nine hydrated limes studied by Bishop contained at least 60 percent of material finer than 10 microns. Quicklimes are very seldom ground to such a high degree of fineness. See footnote 11, p. 422.

[14] Proc. Am. Soc. Testing Materials **33**, II, 553 (1933).

cements probably had the effect of making the specific surfaces of the no. 6 blends slightly greater than those of the other 5 cements. No specific surface determinations were made on the blends of cement no. 6.

(b) METHOD OF PREPARATION

The blends without gypsum were prepared by placing together the properly weighed fractions in a laboratory mill and mixing with wooden balls for a half hour. The same general procedure was used in adding the gypsum to the blends as was used in adding it to the 0–7 fraction. The gypsum was first mixed for one-half hour with one kilogram of 0–7 material in a small mill with a small charge of stone pebbles. This mixture was then transferred to a larger mill; the remainder of the 0–7 and the proper weights of the other fractions were added, and the whole was mixed with the aid of a few wooden balls for one-half hour.

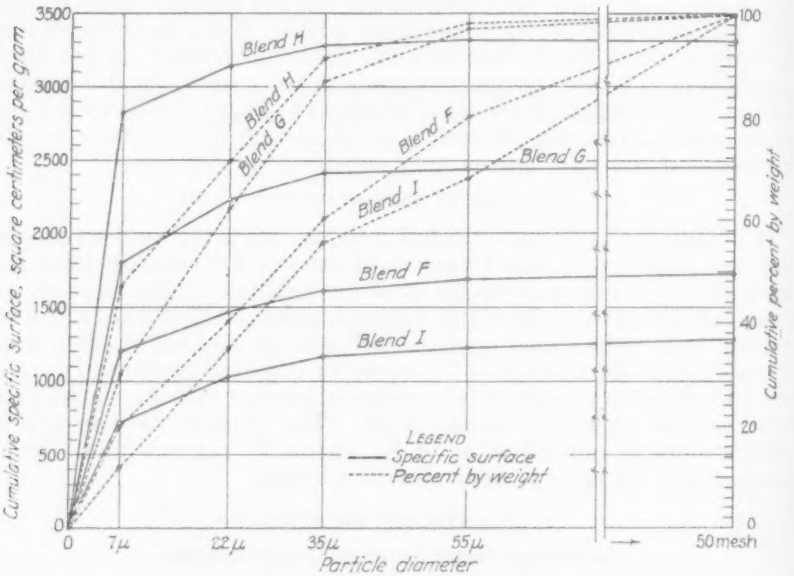


FIGURE 5.—*Specific surface and weight distributions of blends.*

III. DESCRIPTION OF TESTS

Each of the fractions and the four blends prepared from the fractions were tested for consistency, time of set, soundness, tensile and compressive strength. Strength tests were made on 1:3 mortar briquettes and 3- by 6-in. concrete cylinders at 1, 3, 7, and 28 days and 1 year. Three specimens were tested at each age.

The procedures of Federal Specification for Portland Cement, SS–C–191, were followed as closely as possible in making the tests of the neat pastes and the 1:3 mortars. However, only one attempt was made to arrive at a normal consistency, since it was realized that this test could have very little meaning, especially in the case of the individual fractions. Water was added until the operator judged the paste to be of about normal consistency; the Vicat reading was then taken and the pat made irrespective of the reading. The time of

setting was observed by means of Gillmore needles, for the first seven hours, beyond which the time of set was not determined.

In making the mortar specimens an amount of water equal to 15.0 percent by weight of the dry cement was used throughout on the 0–7 micron material. For the other fractions and the four blends this percentage was maintained at 11.0. In the case of some of the coarser fractions it was found necessary to seal the bottoms of the molds with an asphaltic material in order to keep the water from seeping out.

The mix from which the concrete cylinders were made was proportioned 1:2 ¼:3¾ (cement:sand:coarse aggregate) by dry rodded volumes. Potomac River sand with a fineness modulus of 2.84 was used. The coarse aggregate consisted of one part no. 4 to −⅜ in. and one part ⅜ in. to ¾ in. gravel, the fineness modulus being 6.50. The fineness modulus for the combined sand and gravel was 5.1. The cement was assumed to weigh 94 lb./ft.^{3}, although actually there were considerable variations in bulk density between the different fractions and blends. A cement-water ratio, by weight, equal to 1.25 was used throughout on the 0–7 micron material. For the other four fractions and the blends this ratio was maintained at 1.80. Enough water was added to compensate for absorption by both coarse and fine aggregate. The concrete was tamped 25 times in each of three layers as it was placed in 3- by 6-in. tin cans. When the cans had been filled, covers were put on and sealed with asphalt in order to prevent loss of water by evaporation. These cans were then stored at 70±3° F until the time of test, when the cylinders were removed from the cans and capped with plaster of paris.

IV. GENERAL NOTES ON PROPERTIES OTHER THAN STRENGTH

1. CONSISTENCY AND WORKING QUALITIES

(a) FRACTIONS

As was to be expected, the individual fractions were found to vary greatly in properties such as ability to hold water, plasticity, and ease of molding and troweling. The extent of some of these variations can be observed in table 3. The 0–7 fraction, having a very high surface, fell in a class by itself; the other four fractions ranged rather uniformly from the 7–22 fraction, which was not vastly different from an ordinary portland cement, to the >55 fraction which behaved very much like a fine sand.

The 0–7 fraction required a very high percentage of water for neat pastes of approximately normal consistency, and it was found necessary to use very low cement-water ratios in order to obtain workable mortars and concretes. The resulting pastes, mortars, and concretes were in all cases very plastic. They were also characterized by an extreme stickiness, which made the neat pastes and mortars difficult to trowel. There were in no cases any signs of water segregation from this material.

In rather marked contrast to this behavior of the 0–7 micron material, the four coarser fractions were all more or less deficient in the power to hold water and also in plasticity and good working qualities. When the neat paste made from the 7–22 fraction was put in the Vicat ring a very thin paste would usually come to the top and some would seep out under the bottom of the ring. A

similar effect was noticed in the mortars and concretes. This fraction also appeared somewhat harsh and was slightly harder to mix than a whole cement.

TABLE 3.—*Neat-paste data*

Fraction or blend	Cement no.	No gypsum						3.6 percent of gypsum					
		H_2O	Penetration of needle		Time of set		Soundness	H_2O	Penetration of needle		Time of set		Soundness
			A [1]	B [2]	Initial	Final			A [1]	B [2]	Initial	Final	
		Percent	mm	mm	*Hour*	*Hour*		*Percent*	mm	mm	*Hour*	*Hour*	
0–7μ	1	50.0	40	30	4.5	8	Cracked [3]	47.8	13	10	4.5	7.5	Cracked.[3]
	2	50.0	6	4	3.5	7–23	Cracked [3]	42.0	10	14	1	5	OK.
	3	45.4	7	1	2.5	7	OK	44.0	40	38	4	8	OK.
	4	40.0	5	3	1	8	Cracked [3]	43.4	40	15	1	8	Cracked.[3]
	[4] 5							54.0	12	10	1.5	5	OK.
	6	47.0	13	5	4	7	OK	47.0	4	2	4.5	7	OK.
7–22μ	1	38.4	35	15	8	7–23	OK	36.0	32	40	8	8–23	OK.
	2	35.0	11	14	6	7–23	Cracked [3]	33.0	35	40	5	7–24	OK.
	3	38.0	40	40	8	8–23	OK	36.0	38	40	7	7–24	OK.
	4	36.0	38	30	7–24	36	OK	31.8	32	40	7	7–23	OK.
	5							33.0	24	30	6	7–23	OK.
	6	43.0	12	30	4.5	7.5	OK	43.0	13	10	5	8	OK.
22–35μ	1	32.0	27	10	7–23	28	OK	30.0	22	40	8.5	23	OK.
	2	31.0	10	9	7–23	23	OK	28.0	20	28	7	8–24	OK.
	3	30.0	10	20	1	7–24	OK	28.0	7	15	7	7–23	OK.
	4	28.4	12	20	7–24	30–48	OK	28.0	22	40	7	7–24	OK.
	5							28.0	8	15	6.5	7–23	OK.
	6	47.6	5	7	6.5	7–24	OK	48.0	13	30	6.5	7–23	OK.
35–55μ	1	30.0	3	4	5	23.5	OK	30.0	22	38	7–24	24	OK.
	2	30.0	7	1	8–24	8–24	OK	27.0	12	22	7–23	7–23	OK.
	3	30.0	11	22	7	7–24	OK	29.0	20	35	8	24–48	OK.
	4	28.0	8	15	7–24	48	OK	28.0	30	40	6–22	22	OK.
	5							28.0	17	35	7–23	7–23	OK.
>35μ	6	50.0	2	3	4	23	OK	50.0	16	35	5	23	OK.
>55μ	1	30.0	7	5	5	27	OK	28.0	20	10	7–24	28	OK.
	2	30.0	3	1	8–24	8–24	OK	28.0	25	35	7–23	7–23	OK.
	3	30.0	9	23	7	30–48	OK	29.0	28	35	7–22	30–48	OK.
	4	28.0	3	3	7–24	72	OK	30.0	35	40	6–22	22	OK.
	5							28.0	30	15	6–22	22.5	Warped.
F	1	24.0	30	10	4	23	OK	23.0	9	11	4	7	OK.
	2	23.0	3	1	3	8	OK	23.0	12	25	4	8	OK.
	3	24.0	35	37	.5	6	OK	22.0	11	15	4.5	7–22	OK.
	4	23.0	40	40	2.5	7–23	Cracked [3]	22.0	40	40	4	7–24	OK.
	5							23.0	7	9	4	6.5	OK.
	6							32.4	5	2	4.5	7.5	OK.
G	1	27.6	8	13	2.5	7.5	OK	28.0	10	15	4.5	8	OK.
	2	29.6	7	2	3	8	Cracked [3]	28.0	35	30	3	7	Cracked.[3]
	3	26.0	9	3	.5	6	OK	25.0	8	27	4	8	OK.
	4	24.0	6	3	1.5	7–23	Cracked [3]	24.0	7	10	2.5	7–24	OK.
	5							29.0	9	9	3	5	OK.
	6							35.6	8	3	4.5	7	OK.
H	1	31.4	8	7	2.5	7	OK	32.0	8	7	4	8	OK.
	2	33.0	7	2	3	8	Cracked [3]	29.2	15	15	2	7	OK.
	3	30.0	13	15	.5	6	OK	29.0	12	30	4.5	9	OK.
	4	27.0	10	3	1	22	Cracked [3]	27.0	10	9	1	8	OK.
	5							33.0	6	6	1	2.5	OK.
	6							36.0	6	3	4	7	OK.
I	1	22.0	11	35	5	7–23	OK	22.0	13	13	6.5	9	OK.
	2	23.0	5	2	3	8	OK	22.6	30	32	5	9	OK.
	3	24.0	35	40	1	7–24	OK	22.0	20	38	7	7–24	OK.
	4	21.0	15	5	3	7–22	Cracked [3]	20.0	22	15	5	6–24	OK.
	5							22.0	6	10	5	7.5	OK.
	6							33.0	8	5	5	8	OK.

[1] Standard Vicat needle.
[2] 100 g needle of 5-mm diameter.
[3] Pats developed cracks before attaining final set; no further distortion during steaming.
[4] 6.5-percent of gypsum added to fraction.

These tendencies were very much accentuated in the case of the 22–35 and the 35–55 fractions. The neat pastes made from these fractions would appear quite dry, but when they were put in the Vicat ring practically clear water would rise to the surface and some would run out between the ring and glass plate. Likewise, there would always be a considerable amount of water segregation from the mortars and concretes. As to working qualities, these fractions were always definitely lacking in plasticity, and the pastes, mortars, and concretes were very harsh.

The >55 fraction differed from the 22–35 and 35–55 fractions in that the mortars and concretes made therefrom always appeared much drier and showed much less segregation than those made from the other two fractions. There was not as great a difference in this respect between the neat pastes of these three fractions as there was between the mortars and concretes, there being always a considerable amount of water segregation from the >55 neat pastes. This largest sized fraction was, of course, entirely lacking in plasticity, and it behaved under all conditions very much like a fine sand.

The addition of gypsum to the clinker fractions in some cases made the pastes noticeably smoother, and in a few instances it served to remove a tendency of the pastes to stiffen shortly after the mixing was completed. The 0–7 micron material without gypsum usually showed this tendency to stiffen immediately after mixing, but after the gypsum had been added it no longer did this. This was also true for the four coarser fractions of cements 2 and 3. It can be seen from the neat-paste data of table 3 that the Vicat penetrations are generally greater for the material containing gypsum, although on the average a lower percentage of mixing water was used. The presence of the gypsum had no noticeable effect on the amount of water segregation, except that this segregation was increased in those cases where the plain material had tended to stiffen.

(b) BLENDS OF FRACTIONS

There were also naturally rather wide variations in the working qualities of the blended cements. The two low surface blends, I and F, were quite similar to ordinary portland cements, while the two high surface blends, G and H, resembled high-early-strength cements in their behavior. Blend I was somewhat more harsh than the usual portland cement, and blend H was more plastic and also more sticky than the usual high-early-strength cement. Since medium cement-water ratios were chosen and used for all four of the blends, the I mortars and concretes were rather wet and those of the H blends were somewhat dry. There was a slight amount of water segregation from the blend I concrete mixes of cements 2 and 4 containing gypsum. The concrete mixes of the H blend were in several instances too dry to allow good fabrication of test specimens.

The percentage of water necessary for neat pastes of approximately normal consistency was found to be very nearly directly proportional to specific surface. In figure 6, the average of the percentages used for cements 1 to 4, inclusive, is shown plotted against specific surface. It is seen that a linear relationship exists. This figure also shows that the addition of gypsum made it possible to use a slightly lower percentage of mixing water.

118587—35——5

2. TIME OF SETTING

It is possible that the data on setting time for the individual cements do not have very much quantitative significance because of the large number of variables which entered into the determinations. Neither the amount of water used nor the consistency were kept constant; only one attempt was made in each instance to arrive at a normal consistency, and as the data show, a large percentage of the pastes varied considerably from normal consistency. Another disturbing factor in the case of the fractions was the nonuniformity in the test specimens brought about by water segregation. However, when averages are considered, the data do indicate certain general trends.

The setting times seem to be closely related to specific surface; the greater the surface, the shorter the time of set. In figure 6 the

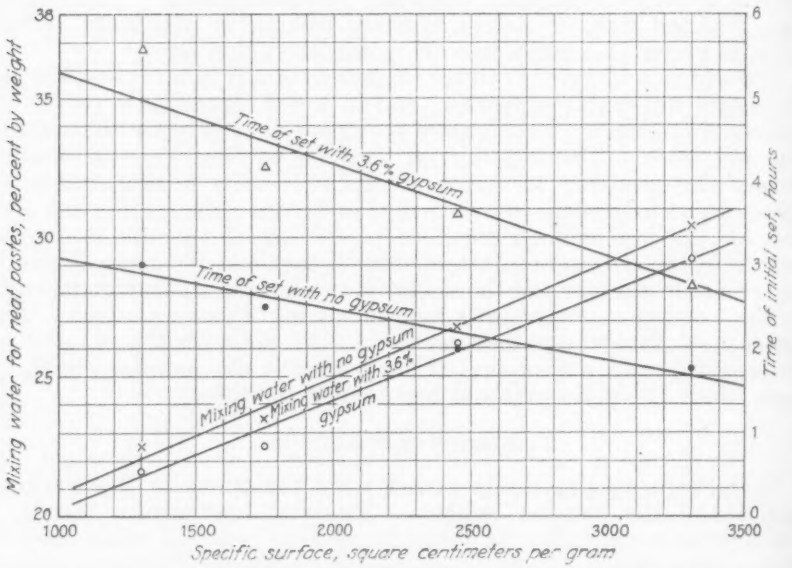


FIGURE 6.—*Averages of mixing water and of times of initial set for blends as a function of specific surface.*

average time of initial set of the blends for cements 1 to 4 is plotted against specific surface. It is seen that the addition of gypsum prolonged the time of initial set. The setting times of the individual fractions were not plotted because they were not determined accurately for the coarser material, but the data show that the time tends to increase as the grain size increases.

The blends of cement no. 3 without gypsum behaved in a rather unexpected manner, especially in view of the results obtained on the individual fractions. Although none of the fractions were quick setting, the four blends all had the initial set within one hour. The lower percentage of water used on the blends may have had something to do with this apparent speeding up of the setting process.

3. SOUNDNESS

If soundness is defined as the ability of a neat-paste pat to withstand 5 hours of steaming without any distortion, there is only one case of unsoundness to report. The pat made from the >55-micron material of the high-early-strength clinker no. 5 (with gypsum added) showed no signs of distortion when placed in the steam chest, but after having been steamed for 5 hours it was warped and beginning to spall. With this one exception, all of the pats survived the steam test without any noticeable ill effects.

There were, however, several instances where the pats developed shrinkage cracks in the damp-storage closet before the final set had been attained, but showed no further distortion in the steam test. Most of these cases of early shrinkage occurred in the materials to which gypsum had not been added, ten out of the thirteen cases in all being found in the "no gypsum" column of table 3. Of the individual fractions, the 0–7 was the one which most frequently developed the shrinkage cracks, and it seems probable that this shrinkage of the fine material was responsible for the similar behavior of the blends in several instances. For example, in the case of cement no. 4 without gypsum, the pats made from the blends developed a considerable number of shrinkage cracks as did the 0–7, although those made from the four other fractions had all remained intact. The same effect was noticed in cement no. 2.

V. DISCUSSION OF STRENGTH DATA

1. INTRODUCTORY AND GENERAL DISCUSSION

In examining the strength data (table 4) there are several factors which should be kept in mind. In the first place, the strengths of the fractions of any one cement should not be compared to each other without considering the variations in their chemical composition. The fractions of cements nos. 2 and 5 are probably sufficiently uniform in composition to allow direct comparisons of strength. The other four cements, however, show variations of 15 percent or more in tricalcium silicate, with corresponding differences in dicalcium silicate. Since the former compound contributes mostly to the early strength and the latter to that at the later ages, these variations would account for a part of the differences between the strengths of the fine and coarse fractions, the whole of which might at first sight be attributed to differences in surface. This positive influence of the silicate distributions is partially vitiated by the higher percentage of hydrated material in the fine fractions as indicated by the ignition loss.

Other factors which ought to be considered in studying the strength data are the differences, shown by the concrete mixes and mortars, in compactability and water retaining capacity. With the exception of the 0–7 fraction the same cement-water ratio was used throughout, and since the size gradations of the fractions and blends varied over a broad range there were naturally wide variations in their working qualities. The gradation of any one fraction or blend, however, was the same for all cements and differences in working qualities resulting from size gradation should be exhibited in like degree by the same fraction or blend of each cement.

TABLE 4.—*Strength data*

NG=No gypsum added to the fraction or blend.
G=3.6 percent of gypsum added.

Fraction or blend	Cement	Cement-water ratio by weight for concrete	Tensile strength in lb per sq in. 1:3 standard sand mortar [3]										Compressive strength in lb per sq in. (3- by 6-in. concrete cylinders)										Flow	
			1 day		3 days		7 days		28 days		1 year		1 day		3 days		7 days		28 days		1 year			
			NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G	NG	G
	1	1.25	215	225	365	375	410	360	415	440	320	370	620	575	1510	1480	1800	1720	2090	1900	2150	2310	33	47
	1	1.80												1050		2070		2360		2460		3060		
	1	1.55																2160		2350				16
	2	1.25	285	230	370	305	405	330	415	365	340	300	800	530	2020	1770	2200	2110	2890	2340	2720	2220	4	45
	2	1.65												1530		2770		2960		3320		3410		10
	2	1.55												1510		2960		3160		3520		3320		9
	2	1.40												1310		2240		2790		3170		3110		10
	3	1.25	225	240	360	330	395	400	410	470	310	325	390	500	1700	1440	1930	1780	2355	2210	2300	2270	37	64
0–7μ	3	1.80												1270		2270		2850		3060		3050		23
	3	1.55																2190		2520				24
	4	1.25	85	40	295	300	300	305	355	365	275	295	170	30	1270	1190	1530	1640	2130	2250	2350	2300	22	45
	1.5	1.25												1280		1550		1700		1930		2020		10
	1.5	1.55		390		380		365		390		300		790		1080		1250		1660		1610		
	2.5	1.25		320		350		365		375		270		890		1720		1910		1930		2100		12
	6	1.25	205	200	255	200	285	250	330	275	255	210	630	550	930	790	1040	1010	1260	1200	1560	1530	42	33
	1	1.80		70	120	245	195	355	405	485	415	430	90	245	735	1440	1510	2510	2810	3630	3400	4200	33	43
	2	1.80	70	110	225	335	315	415	475	530	430	520	75	455	1260	1630	2280	2570	3760	3470	3740	3860	16	41
	3	1.80	40	60	140	240	215	335	385	520	415	485	65	215	785	1210	1660	2190	2860	3380	2790	4000	41	33
	3	1.25												60		500		1070		1760		2690		
	4	1.80		85	145	275	325	385	410	425	445	485	80	260	390	1370	2150	2140	2760	2840	3740	4050	45	36
7–22μ	4	1.25												80		505		770		1110		1920		
	5	1.80		145		295		460		480		405		590		2330		3640		4250		4110		12
	1.5	1.55												325		1370		2320		2740		3350		40
	2.5	1.25												210		820		1600		1870		1950		
	6	1.80	175	205	240	310	255	375	330	400	240	300	790	870	1620	2110	2120	2700	2550	3380	2680	3950	23	17
	1	1.80		30	40	65	85	160	170	360	400	425	30	55	270	530	710	1120	1680	2680	2900	4080	46	52
	2	1.80			40	110	90	215	200	420	370	450	20	125	260	750	1030	1750	2160	3020	3480	3850	19	65
	3	1.80	20		70	50	135	125	200	350	380	355	15	55	320	470	950	1270	2220	2790	3400	4220	33	49
22–35μ	4	1.80			35	90	150	170	295	275	430	445	40	45		680	210	1480	2060	2340	4720	4390	53	38
	5	1.80		40		135		265		440		335		160		1220		2180		3460		3740		14
	6	1.80	40	45	55	70	75	110	145	160	185	195	170	180	350	570	610	890	1270	1500	1520	2510	(4)	24
	1	1.80					45	45	100	240	315	365	10	25	110	230	400	505	1220	1610	2590	3520	41	50
	2	1.80			30		65	45	115	260	320	380		35	105	355	615	875	2160	2360	2940	3500	25	47
	3	1.80			35	25	75	30	115	175	300	360		20	105	145	765	605	2265	1810	3070	3380	36	36
35–55μ	4	1.80				30	55	55	145	155	310	370		20	5	200	20	515	1580	1280	4320	2980	45	23
	5	1.80				30		105		315		335		55		490		1070		2560		2540		17
>35μ	6	1.80		25		35	40	40	65	80	180	175	40	50	80	140	110	180	210	370	580	1130	(4)	(4)

>35μ	1	1.80																									
	2	1.80																									
	3	1.80																									
	4	1.80																									
	5	1.80																									
	6	1.80		25		30 35	40	105 40	65	315 80	180	385 175	40	50	80	140	110	180	210	370	580	1130	(4)	(4)			
>55 μ	1	1.80					20			65	315	210		10	15	45	90	80	520	370	1270	1980	40	35			
	2	1.80						25	50	125	135	305		15	25	100	140	280	525	870	1840	2240	36	29			
	3	1.80					25	25	45	30	155	250				35	130	75	650	435	2180	2240	32	40			
	4	1.80						30	60	55	180	270		10		55	10	175	580	450	2690	1750	44	24			
	5	1.80								100		235		15		120		235		1000		2060		23			
F	1	1.80		70	125	185	200	300	300	400	350	320	55	195	705	1190	1520	2190	2470	2240	2970	3520	46	53			
	2	1.80	30	90	155	215	240	295	380	400	335	420	90	275	725	850	1780	1950	2590	2310	3620	3470	15	50			
	3	1.80	40	45	110	150	175	235	325	400	345	345	70	150	725	810	1420	1520	2360	2640	3460	3210	52	50			
	4	1.80		30	95	140	180	200	285	310	370	370	10	185	280	665	960	1030	2480	2160	3940	3430	53	25			
	5	1.80		110		220		335		375		300		310		1250		2310		3070		3620		14			
	6	1.80		100		170		210		300		345		475		835		1190		2140		3660		17			
G	1	1.80	90	190	225	300	335	420	400	500	425	460	150	540	1560	1900	2440	2710	3200	3060	3760	4340	25	32			
	2	1.80	110	190	265	280	350	370	425	455	410	410	155	470	1320	1960	2530	2660	3260	3640	3890	4320	10	37			
	3	1.80	90	115	210	265	335	320	450	455	375	425	155	430	1230	1600	1990	2320	2140	3420	3430	4200	44	30			
	4	1.80		80	185	260	270	305	340	410	370	450	15	280	740	1190	1770	1940	2760	2610	4450	3860	37	23			
	5	1.80		150		380		410		445		370		390		2080		2810		3690		3490		18			
	6	1.80		175		280		310		390		435		705		1370		2010		3010		3740		10			
H	1	1.80	145	275	310	395	430	460	455	495	435	495	280	710	1970	2320	2620	2870	3320	3470	3860	3770	20	20			
	2	1.80	200	185	365	310	410	430	485	490	420	395	360	615	2020	2330	2600	2620	3750	3620	3830	3970	10	21			
	3	1.80	170	200	275	360	405	410	460	460	395	405	245	530	1600	2100	1990	3000	2520	3510	2910	3880	28	28			
	4	1.80	35	130	235	285	320	350	375	465	405	430	45	525	1290	1420	2020	2320	3320	3120	4280	3900	19	20			
	5	1.80		260		365		435		430		355		340		1590		1720		1690		1820		(4)			
	[2] 5	1.80		340		390		405		445		355		1190		2900		3180		3910		3920		14			
	6	1.80		235		345		360		390		340		930		1760		2340		3410		3830		13			
																								50			
I	1	1.80	30	45	85	140	160	240	255	365	320	390	30	95	430	780	1050	1550	2240	2220	2870	3170	54	59			
	2	1.80	25	65	120	190	195	255	300	360	310	340	40	240	570	1010	1310	1640	2460	2830	3440	3860	20				
	3	1.80	20	25	90	100	130	220	265	330	345	310	35	115	420	650	1180	1460	1980	2460	2590	3690	49	42			
	4	1.80		40	55	120	145	170	260	290	350	400	5	140	110	615	730	1060	1980	1760	3940	3510	65	25			
	5	1.80		80		200		285		360		260		270		1130		1960		2820		3260		13			
	6	1.80		95		160		195		315		355		325		815		1050		1830		3360		25			
N	1	1.80	30	120	100	190	160	225	205	270	190	230	55	195	260	590	490	830	715	950	755	1160	(4)	(4)			
	2	1.80	60	115	145	190	170	230	190	270	165	270	70	280	310	880	465	1090	610	1570	655	1840	(4)	(4)			
	3	1.80	55	80	105	145	155	225	210	240	185	220	40	175	220	575	380	985	555	1120	765	1240	(4)	(4)			
	4	1.80		50	105	175	160	210	225	270	250	245		175	210	475	570	630	960	805	1300	1320	(4)	(4)			
	5	1.80		100		180		200		240		175		130		565		790		975		865		(4)			
	6	1.80		115		140		170		205		120		245		610		775		1080		1440		(4)			
O	1	1.80	50	95	100	135	130	180	145	185	90	155	60	140	235	310	310	600	430	580	400	745	(4)	(4)			
	2	1.80	85	80	130	165	160	200	175	215	140	165	70	180	215	405	260	765	420	760	490	1110	(4)	(4)			
	3	1.80	70	85	110	130	115	170	165	205	80	150	35	145	180	345	225	515	190	765	295	865	(4)	(4)			
	4	1.80		45	105	135	120	180	120	140	130	165	10	140	220	305	410	340	410	540	460	720	(4)	(4)			
	5	1.80		90		110		125		140		100		65		375		300		440		410		(4)			
	6	1.80		110		135		140		165		120		210		375		500		700		750		(4)			

[1] 10 percent of gypsum added to fraction.
[2] 6.5 percent of gypsum added to fraction.
[3] A water-cement ratio of 1.67 was maintained in making the 0-7 mortar briquets; for the mortars of the other fractions and the blends this ratio was maintained at 2.27.
[4] Too dry; crumbled.

The concrete cylinders made from the three fractions of material finer than 35 microns had smooth glossy surfaces in all cases where the mix had remained workable until the molding was completed. On the other hand, the cylinders made from the two largest sized fractions always had rough surfaces and appeared to be much more porous. When the wet concretes made from the 22–35 and 35–55 fractions were being tamped into the molds a considerable layer of water would usually rise to the surface. Although the water in all cases had been taken up into the body of the specimens before the twenty-four hour tests were made, its occurrence might give rise to some question as to whether the cement-water ratio for these specimens actually was the ratio of the weights of cement to water in the concrete mix or whether the concrete was of a higher ratio and contained a certain amount of absorbed water. The analysis of the data, which will follow, indicates that these differences in ability to hold water did not change the "effective" cement-water ratios appreciably.

The concrete mix of the I blend was always rather wet, while that of the H blend was always somewhat dry and hard to work. Since the mixes of the I blend showed signs of water segregation in only two cases and could always be molded into good cylinders, the strength data obtained for this blend should not be open to much criticism. The concrete mixes of the H blend, however, in the majority of cases were sufficiently stiff to leave some room for question as to the compactness of the cylinders molded therefrom, even when there was no noticeable honeycombing. The cylinders made from the H blend usually did not have as smooth glossy surfaces as those made from the other three blends.

In addition to the variations in working qualities resulting from size gradation described in the above paragraphs, there were also variations peculiar to individual cements. The fine fractions and higher-surface blends of ground clinkers nos. 2 and 3, without the addition of gypsum, tended to stiffen immediately after the mixing was completed and the cylinders molded from them showed considerable honeycombing. The coarser fractions and lower-surface blends of these cements, however, were not as much affected by the tendency to stiffen and usually molded into good cylinders. A direct comparison of the strengths in these instances, therefore, would be unfair to the finer fractions and the two fine blends. The same tendency was shown by the high-early-strength clinker, no. 5, even after the addition of 3.6 percent of gypsum. For this brand it was necessary to add 10 percent of gypsum to the 0–7 fraction and 6.5 percent to the H blend in order to obtain cylinders free from honeycombing with the regular 1.25 and 1.80 cement-water ratios, respectively.

In this connection the N and O blends, which appear at the bottom of table 4 but have not been previously mentioned, might be discussed. In designing the mortars and concrete mixes from which the test specimens labeled N and O, respectively, were fabricated an attempt was made to use the weights of blends G and H, which would give the same total cement surface in the resulting mixes as that contained in the I-blend mixes. Thus, while both the N and O mixes contained the same total cement surface as the blend I mixes, they actually contained much less cement by weight. On the average the N mixes contained about 55 percent and the O mixes about 45 percent by

weight, of the cement contained in the blend I mixes. The exact proportions to be used in each instance were calculated from the specific surfaces as determined in the Wagner turbidimeter. It was believed that these tests might yield some direct evidence as to the relation between specific surface and strength. However, in order that comparable figures might be obtained, it was essential that the same cement-water ratios should be used for these mixes as for the four blends, and this requirement led to difficulties. The amount of cement was so much decreased in proportion to the aggregate that the quantity of water required by the regular ratio was not sufficient to produce a workable mix. The mortars and the concrete mixes were in all cases of about the consistency of moist earth and there was but very little cohesion. The concrete cylinders had very rough surfaces and were obviously not compact. It is possible, therefore, that the results obtained from these mixes do not have much quantitative significance, but they do indicate certain trends in a qualitative way, which will be subsequently considered.

Since only three strength specimens were tested at each age it was not possible to obtain any very exact measures of the precision of the strength determinations. The "standard deviation" of the mean of three values as given by the formula

$$\sqrt{\frac{v^2}{n\,(n-1)}}$$

where v is the deviation of an observation from the arithmetical mean and n is equal to the number of observations, or 3 in this case, was calculated for the compressive strengths obtained at the ages 1 day, 7 days, and 1 year in all tests of cements 1 to 4, inclusive. The values obtained, expressed as percentages of the strengths, ranged from 2.3 to 6.0 with averages of 4.8, 4.1, and 4.4 for the ages 1 day, 7 days, and 1 year, respectively.

If the factors considered above are borne in mind, an examination of the data in table 4 will bring out a number of generalities. In the first place it can be seen that the strengths are closely, although not directly, related to specific surface. The relation is much more distinct at the early ages than at the latter. This, of course, is as would be expected since the rate of reaction must be closely related to the surface area in contact with the water, and as the reaction proceeds the effective surface areas change. The relation will be further considered in the theoretical discussion.

Another effect which is easily noticed is that produced by the addition of gypsum to the clinker. The strengths were, in general, considerably increased by this addition, particularly at the early ages. The 0–7 fraction is an exception to the rule, because in almost all instances the strength of this material shows a decrease after the gypsum has been added. Another exception to the rule is found in the case of clinker no. 4. The addition of gypsum caused a large increase in all of the strengths at the early ages, but at the age of one year, and even at 28 days for the blends, the compressive strengths of the plain ground-clinker specimens were considerably higher. The order of the tensile strengths remained unchanged.

The correlation between tensile and compressive strengths is as good as might be expected. The same general tendencies are exhibited by each group of data. The falling off in one-year tensile strength is a common occurrence with tensile specimens stored in water.

2. THEORETICAL CONSIDERATIONS

The question that has probably been the subject of the most controversy in discussions of the effect of fineness on strength pertains to the importance of the very finest material, or the "flour", as it is sometimes called. Several investigators have studied fractions of the finest material, such as that finer than 5 or 10 microns, but in testing these fractions they have always had to use more water than in the whole cements or the coarser fractions, and therefore have been unable to obtain comparable results. The same difficulties were encountered in this investigation. Several attempts were made at testing the 0–7 and 7–22 fractions with the same water ratio, but it was not possible in any case to obtain good specimens for both materials.

The results of some of the attempts made at reaching a compromise are shown in table 4. In the case of cement no. 1 it is seen that the strengths of the 0–7 are considerably higher at 7 and 28 days with the cement-water ratio of 1.55 than with the regular 1.25 ratio. They show still higher strengths with the ratio 1.80, although this mix was so dry when molded that it was difficult to see how the specimens could develop any appreciable strength. The data available on cement no. 2 probably illustrate the effect better than those of any of the others. Here three intermediate water ratios were tried. The strengths increase regularly up to the ratio 1.65, when they begin to fall off. The cylinders made with this highest ratio were very badly honeycombed, and it was rather surprising that they developed as high strengths as they did. With cement no. 5 an attempt was made to use the same intermediate ratio for both the 0–7 and the 7–22 fractions. The strengths of both fractions were lowered considerably, the 7–22 remaining the higher. This, however, was not a fair test, because the fine fraction of no. 5 heated up and became dry even with the 1.25 cement-water ratio, and when the water was decreased it became so dry that there was practically no cohesion at all. When tests were made on the 7–22 fraction of cements 3, 4, and 5, using the same amount of water as was used on the 0–7 material, the strengths developed in most instances were less than half as high as those which were obtained with the higher ratio, although in every instance there had been a considerable amount of water at the tops of the cans, even at 28 days, so that the "effective" ratio really was higher than 1.25.

If we assume that the relation between the cement-water ratio and strength is one which approximates a straight line and extrapolate to the ratio 1.80, we see that the fine material has a very high potential strength. It is known that for ordinary cements the strength is very nearly directly proportional to this ratio, within the workable range, so that there is some justification for such a procedure. There are not enough points within the workable range to establish a line, but it can be seen that the strengths increase rapidly with increasing cement-water ratio, until the point is reached where the effect of poor fabrication becomes apparent. All the evidence from these tests,

therefore, points to the conclusion that the 0–7 micron material has a very high intrinsic worth as far as strength conferring properties are concerned.

There is still another and entirely different way in which the problem may be approached on the basis of the data in table 4. If we assume that the contributions of the individual fractions to the strengths of the blends are additive, it is possible to arrive algebraically at the "apparent strength" of the fine fraction. Thus if a, b, c, d, and e are the strengths of the five fractions of a given cement and f, g, h, and i are the strengths obtained by the blends, we can write down the equations

$$P_{(0-7)F}a+P_{(7-22)F}b+P_{(22-35)F}c+P_{(35-55)F}d+P_{(>55)F}e=100f$$

$$P_{(0-7)G}a+P_{(7-22)G}b+P_{(22-35)G}c+P_{(35-55)G}d+P_{(>55)G}e=100g$$

where the P's refer to the percentages of the fractions in the blends. For example $P_{(0-7)F}$ represents the percentage of the 0–7 material contained in blend F. These equations should hold if the above assumption is sound and if all the fractions had been tested in the same way. Since four of the fractions were tested under similar conditions, we can, by proceeding on this assumption, use these equations to calculate the contribution of the 0–7 fraction to the strengths of the blends. The equations are then written:

$$a=\frac{100f-P_{(7-22)F}b-P_{(22-35)F}c-P_{(35-55)F}d-P_{(>55)F}e}{P_{(0-7)F}} \text{ etc.,}$$

Apparent compressive strengths have been calculated according to this method and are presented in tables 5 and 6. Table 5, which is a tabulation of the seven-day strengths as calculated from each of the blends, is included in order to give an idea of the kind of agreement found between the four different values which it was possible to calculate for each age. Table 6 is a summary of the calculated strengths. The values presented in table 6 are the weighted means, or the most

TABLE 5.—*Calculated compressive strength of 0–7 micron fraction at seven days*

Cement no.	Strength in lb/in.² calculated from strength of blends				
	F	G	H	I	Arithmetic mean
1 (No gypsum	4900	5770	4450	4000	4780
1 (Gypsum	6735	5240	4270	5470	5430
2 (No gypsum	4850	4920	3830	3740	4340
2 (Gypsum	4275	4330	3400	4120	4030
3 (No gypsum	3600	3810	2840	3890	3540
3 (Gypsum	3460	4130	4640	5000	4310
4 (No gypsum	2425	3420	3080	1580	2630
4 (Gypsum	850	2760	3150	1240	2000
5 Gypsum	4420	3270	3810	3920	3860
6 Gypsum	2000	3000	3190	1430	2400

TABLE 6.—*Probable means of compressive strengths* (lb/in.²) *of 0–7 fraction as calculated from strengths of blends,* F, G, H, *and* I

Cement no.	Strength at various ages (with, G, and without, NG, gypsum)									
	1 day		3 days		7 days		28 days		1 year	
	NG	G	NG	G	NG	G	NG	G	NG	G
1	270	990	3160	3780	4810	5150	5430	3800	5010	4060
2	420	880	2740	2830	4290	3880	4700	4200	4800	4260
3	340	740	2620	3040	3330	4300	2590	4640	3470	3970
4	-------	680	1700	1580	2880	2390	4540	3720	4130	3950
5	-------	590	-------	2130	-------	3820	-------	4150	-------	4160
6	-------	1160	-------	1800	-------	2720	-------	4990	-------	5980

probable means of the four calculated values. The arithmetic means do not represent the best values because the strengths as calculated from any two different blends are susceptible of quite different errors. The standard deviation of each calculated value was obtained roughly by assuming a standard deviation of 5 percent in all of the strength determinations, calculating the averages of the standard deviations of the strength determinations for each age in pounds per square inch from the averages of all the compressive strengths for that age, and making use of the general equation

$$(du)^2=\left(\frac{\delta u}{\delta a_1}da_1\right)^2+\left(\frac{\delta u}{\delta a_2}da_2\right)^2+\text{------},$$

where

$$u=f(a_1, a_2, \text{------}),$$

and du is the standard deviation of u brought about by the joint occurrence of the errors da_1, da_2. . . . The standard deviations so calculated are given in table 7. The values given in table 6 were obtained by weighting each strength value, as calculated, by the reciprocal of its standard deviation squared, and thus calculating the weighted mean, or the most probable mean, of the four values. The figures given in table 7 are not measures of the actual precision of the calculated values and should be considered only as indicating the relative precision of the four values calculated for any one age.

The manner of increase with age and also the actual magnitude of the calculated strengths given in table 6 suggest that these values are possibly good measures of the actual contributions of the 0–7 micron material to the strengths of the blended cements. One would expect the 0–7 fraction to be almost completely hydrous at the end of 7 days. In most instances the calculated strengths do not show very large increases after 7 days, although the blended cements increase considerably in strength between 7 and 28 days. At 1 year the calculated strengths of the 0–7 are on the average about equal to the observed strengths of the 7–22 fraction, and this is what would be expected since both materials should be very nearly completely hydrous at this age. In any case it seems logical to believe that these calculated strengths indicate the actual worth of the fine material much more closely than the strength data obtained with the low cement-water ratio. Further evidence pointing to this conclusion will be brought out by an attempt to find a direct relation between strength and some function of particle size distribution.

TABLE 7.—*Standard deviations of calculated strengths of 0–7 micron fraction*

Age	Standard deviation in lb/in.² of value calculated from blend			
	F	G	H	I
1 day	70	85	80	95
3 days	250	295	210	390
7 days	450	430	310	660
28 days	650	580	390	1,060
1 year	930	720	430	1,560

The best-known function of size distribution is surface area per unit weight, or specific surface. The belief was once held quite generally that strength at any given age was very nearly a direct function of the original specific surface of the cement. The results of this and other investigations show that if both fractions and blends are considered this relation holds approximately only for the very early ages.

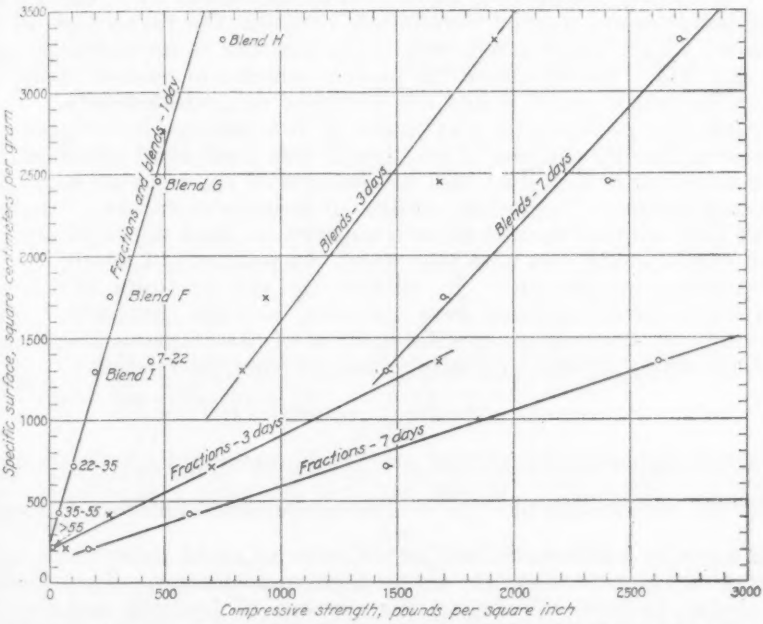


FIGURE 7.—*Averages of compressive strengths of fractions and blends of six cements as a function of specific surface.*

In figure 7 the averages of the compressive strengths for the ages 1 day, 3 days, and 7 days are plotted against specific surface. At the age of 1 day it is possible to visualize a single line through the points. At 3 days the points are much more scattered and the possibility of two distinct curves is suggested. At 7 days it is clearly seen that two distinct curves are obtained, one for the blends and one for the individual fractions. A little consideration will show that this is what would be expected. The rate of reaction must at all times be closely related to the surface of the anhydrous material in contact with the

water. At the age of 1 day the water has not yet penetrated very deeply and the effective specific surfaces have not been appreciably changed so that the strength is very nearly directly proportional to the original specific surface. However, at 3 days much of the fine material in the blends has been rendered completely hydrous so that the effective specific surfaces and therefore also the rates of reaction of the blends have decreased considerably, while the fractions, not containing any fine material, are still being used at a rate not much reduced from the original. This is quite likely the explanation of the fact that the 7–22 fraction, for instance, shows a higher strength at 3 days than blend F, although the original specific surface of the fraction is lower than that of the blend. The same effect, of course, is further accentuated at 28 days.

This explanation of the failure of specific surface to show a direct relation to strength immediately suggests another possible function of gradation. If the rate of strength development is related to the rate of reaction, the strength at any age must be related to the percentage of hydrous material at that age. Eiger,[15] measuring the rate of reaction by the microscopical method developed by Anderegg and Hubbell,[16] found a good correlation between the percentage of the cement which had reacted with water and the compressive strength of concrete. He calculated the percent which had reacted at any age from the rate of reaction and the particle-size gradation data.

Although no attempt was made in the present investigation to measure directly the rate of reaction, it was possible to calculate from the size-distribution data the percentages of the cements which had become hydrous[17] for definite depths of water penetration. Strengths were then plotted against these quantities for each depth of penetration until a depth was found for which the points most nearly approximated a straight line. In calculating the amounts of hydrous material, perfect spheres were assumed, average diameters[18] corresponding to the original specific surfaces of the fractions chosen, and the amount of hydrous material obtained from the relation

$$\text{Percentage of hydrous material} = 100\frac{d_1^3 - d_2^3}{d_1^3},$$

where d_1 represents the original average diameter and d_2 is the diameter after the penetration of $\frac{d_1 - d_2}{2}$. The computation for the 0–7 fraction was made by a differential method in order to avoid introducing more errors than necessary in these high percentages. The method consisted in first calculating the percent of hydrous material for a penetration of one-tenth micron, then taking a new average diameter and finding the percentage of the remainder, which became hydrous during another tenth-micron penetration, calculating the new remainder, and continuing the process to the desired depth. The values for the blends were obtained directly from those of the fractions by calculation from the percentage compositions.

Table 8 gives the calculated percentages of hydrous material for six depths of penetration, and in figures 8 and 9 the 7-day tensile and

[15] A. Eiger, Tonind.Ztg. **56**, 532, 558 (1932).
[16] Proc.Am.Soc.Testing Materials **29**, II, 554 (1929).
[17] By hydrous material is meant that portion of the cement into which water has penetrated without any implication as to the progress of the resulting chemical reactions or the composition of the resulting products.
[18] See footnote to table 8.

compressive strengths of cement no. 2 are shown plotted against the values calculated for a penetration of 1.5 microns. Cement no. 2 was chosen because of the uniform compound compositions of the fractions. Some of the other cements show better relationships at this age. For instance, the 7-day tensile and compressive strengths of cement no. 1 show much smaller deviations from straight lines when plotted against the hydrous material for a penetration of 1.5 microns. At 3 days the correlations are in general better than at 7 days, and the compressive strengths of cement no. 2 for this age show a very good relationship to the calculated values for a penetration of 1 micron. At ages later than 7 days the points are much more scattered, due possibly to larger deviations entering into the strengths themselves as well as to the necessarily increasing errors in the calculated percentages of hydrous material, but the tendency towards straight line relationships remains apparent. The averages of the 28-day compressive strengths of the six cements correlate very well with the calculated values for a penetration of 4 microns, as can be seen in figure 9.

TABLE 8.—*Calculated amounts of hydrous material*

Fraction or blend	Percentage hydrous for penetration of					
	0.5 μ	1μ	1.5μ	2μ	4μ	10μ
0–7μ	61	87	97	99	100	100
7–22μ	20	36	50	61	92	100
22–35μ	11	20	29	37	65	98
35–55μ	6	13	18	24	44	83
7 55μ	3	6	10	13	24	52
F	20	33	41	47	65	87
G	28	44	54	62	81	96
H	36	55	65	71	86	98
I	16	27	34	40	60	82

NOTE.—The diameters used in making the calculations were 3.5, 14, 27, 45, and 91 microns for the 0–7, 7–22, 22–35, 35–55 and <55 fractions, respectively. These values were obtained by substituting the specific surface as calculated from microscopical distribution counts for *ss* in the equation

$$d=\frac{19050}{ss},$$

where ss is the surface in cm² of 1 gram of particles of diameter *d* microns and density 3.15, and 19050 is a constant, which is equal to the surface in cm² of 1 gram of spherical particles of diameter 1 micron and density 3.15. This diameter, which might be termed the "equivalent-surface" diameter, is also given by the equation

$$d=\frac{\Sigma nd^3}{\Sigma nd^2},$$

where *n* is the number of particles of diameter *d* microns in the representative slide.

A comparison of figure 7 with figures 8 and 9 shows that the percent of hydrous material, or, if more rigor be desired, the function of particle-size distribution, which has been called "percent of hydrous material", is a much more fundamental function than the specific surface insofar as strength relationships are concerned. Whereas the strength is closely related to specific surface only when but one type of distribution is present, it is directly related to the new function regardless of the kind of distribution. The fact that the strengths of the fractions fall on the same line as those of the blends tends to prove that the calculated quantities are at least proportional to the amount of hydrous material. There must be some physical cause

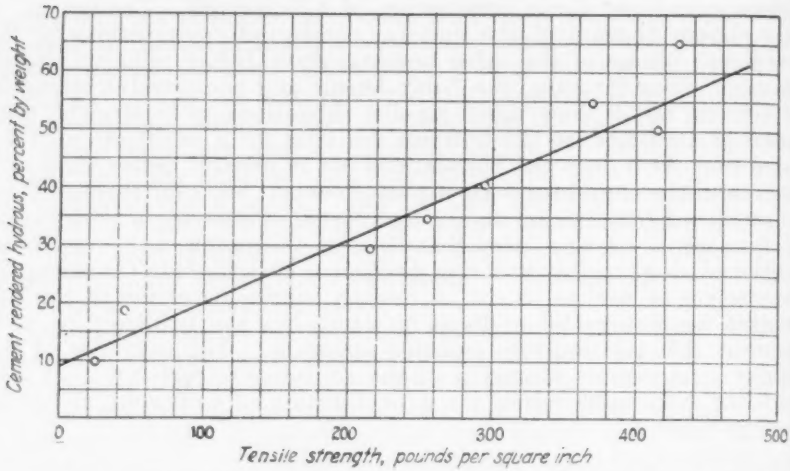


FIGURE 8.—*Tensile strengths of fractions and blends of cement no. 2 at 7 days as a function of the percent of the cement rendered hydrous by a water penetration of 1.5 microns.*

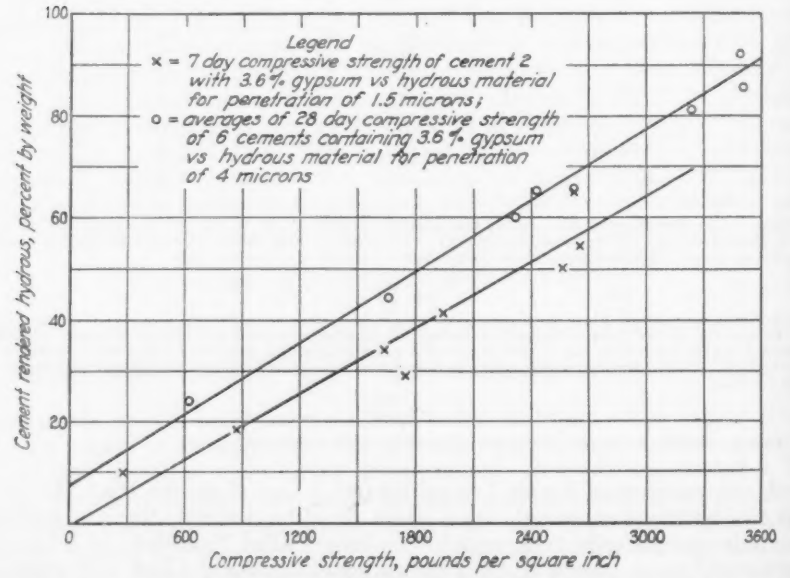


FIGURE 9.—*Averages of 28-day compressive strengths of both fractions and blends made from the six cements as a function of the percent of cement rendered hydrous by a water penetration of 4 microns, and the 7-day compressive strengths of fractions and blends made from cement no. 2 as a function of cement rendered hydrous by a water penetration of 1.5 microns.*

underlying a relationship so fundamental and it is logical to suppose that strength is proportional to the hydrous material. It is interesting to note in this connection that the calculated "apparent strengths" of the 0–7 fraction in most cases come very close to falling on the hydrous material versus strength line, thus affording additional proof of the validity of the assumptions made in each instance.

It is possible to deduce several postulates from the fact that the strengths are related to the calculated percentages of hydrous material. For one thing it shows that the size distribution of the cement particles, of itself, has very little to do with the strength of concrete. A fraction containing only particles within a narrow size range will produce the same strength of concrete as a whole cement containing all sizes of particles if the amount of hydrous material is the same in each instance.

Another possible deduction is that the 0–7 fraction has the same intrinsic worth as any other. It has been maintained by some investigators that particles below a certain size, such as 4 microns, are of no value; but if this had been the case the relationships found would not have obtained. The amounts of hydrous material for the blends were deduced by summing up the contributions of the individual fractions, allowing weights in proportion to the volume for particles of all sizes, and since the 0–7 fraction usually contributed the most to this sum, the fact that the strengths of the blends did fall on the line shows that all of the 0–7 micron particles must have contributed to the strength according to their sizes. The 0–7 fraction contributes more to the strength of concrete, at least at the early ages, than any of the others by virtue of the fact that all of the particles become completely hydrous in a very short time.

From the fact that the amount of hydrous material for the blends of any one cement was obtained by taking the sums of the products of the values for the fractions and the percentages of the respective fractions in the blends, together with the fact that the amount of hydrous material was found to be proportional to the strength, it follows that the strength values are also additive, as was originally assumed in calculating the "apparent strengths" of the 0–7 fraction.

It, of course, must be kept in mind that the conclusions and deductions drawn from this analysis are to be accepted only with reservations. The authors do not insist that the actual amounts of the cements which had become hydrous were equal to those which were calculated and plotted against the strengths. The calculated quantities are rough approximations of the amounts of cement which would have been rendered hydrous by a uniform water penetration of all particles to the assumed depth. The fact that these quantities show direct relations to the observed strengths indicates that they are probably good approximations of the actual amounts of hydrous material. It is realized that other factors might have contributed to bring about this observed relationship. It might also be pointed out that these conclusions apply only to the results of these particular tests as made. Whether or not they would apply for different storage conditions or for tests made with different mixes or cement-water ratios is a matter for conjecture.

The data from the N and O mixes were not used in any of the calculations or correlations. Only a brief inspection is necessary to

show that these data fall in a class by themselves and would not have fitted in with the other data. For example, the compressive strength of the N cylinders at 28 days should have been about 55 percent of that of the G-blend cylinders in order for the strength to be proportional to the hydrous material; actually the averages of the N and G compressive strengths for all six cements were 1,080 and 3,240 pounds per square inch, respectively. Likewise, the O mix yielded concrete, on the average, of only 20 percent of the strength of the H-blend concrete at 28 days, although the percentage should have been about 45 according to the proportionality requirement. It would seem that these large discrepancies must be attributed to the poor working qualities of the N and O mixes, which made it impossible to mold good test specimens. The strength of concrete could be expected, logically, to be closely related, within a certain range, to the weight of cement in the concrete mix, if the cement-water ratio were kept constant. As the proportion of cement and water is reduced, however, a point must necessarily be reached where all semblance of proportionality between amount of cement and strength must cease to exist. The tensile- and compressive-strength data of the N and O mixes, taken together, serve to illustrate this idea. The proportions, by weight, of cement to sand in the N and G mortars were 1:5.4 and 1:3, respectively. The proportions, by weight, of cement to total aggregate in the N and G concrete mixes were 1:11.9 and 1:6.6, respectively. The N tensile strengths are on the average very nearly equal to 55 percent of those of the G blend, while the N compressive strengths are only about 30 percent of those of the G blend, as indicated above. It therefore seems possible that, while the proportion of aggregate to cement in the concrete mixes was made too high, the proportion of sand to cement in the mortars was not so great as to render the supposed relationship between strength and amount of cement invalid. The existence of a critical point in this relationship is further suggested by the fact the O tensile strengths, on the average, are considerably less than 45 percent of those of the H blend.

When the N and O strength data are compared to those of blend I, some pecularities are found which are not easily explained. The N and O test specimens theoretically contained the same total cement surface as the I specimens and might therefore have been expected to show about the same 1-day strengths. Actually, almost all of the N and many of the O 1-day strengths are considerably higher than those of blend I. It is possible that the reduction of the proportions of cement to aggregate may have had the effect of changing the cement-water ratio so as to make the "effective ratio" higher than the actual ratio of the weight of cement to that of water, although allowance was made in designing the mixes for absorption by the aggregate.

As an appendix to the foregoing discussion, there are certain mathematical deductions which might be added because of their interest as curiosa rather than for any direct bearing which they might have upon the problem in hand. If we assume a spherical cement particle of radius r and let it be uniformly hydrous to a depth such that the radius of the anhydrous material will have been reduced

from the original by the amount x, we can express the decimal part by weight which has become hydrous as equal to

$$\frac{r^3-(r-x)^3}{r^3}$$

Calling this part H and differentiating with respect to time, we obtain the equation

$$\frac{dH}{dt}=\frac{3}{r^3}(r-x)^2\frac{dx}{dt} \tag{1}$$

This equation shows that the rate of becoming hydrous, $\frac{dH}{dt}$, of a spherical particle of radius r at any time, t, is dependent upon the linear rate of advance of the hydrated film, $\frac{dx}{dt}$, and upon the depth of penetration, x. If x and $\frac{dx}{dt}$ were known for any time, t, it would be possible to calculate the rate of change to the hydrous state for that time by means of the above equation.

The data on four cements published by Anderegg and Hubbell [19] show that these particular cements, as tested, hydrated in such a way that the depth of penetration became a linear function of the logarithm of the time after 7 days. For example,[20] the relationship between penetration and time for their portland cement "A", with no gypsum addition, can be very nearly expressed by the relation

$$x=3\log_{10}t, \tag{2}$$

when x is the depth of penetration in microns and t is the time of hydration in days. This relationship very nearly obtained for five ages, from 41 hours to 270 days, at which hydration measurements were made. Differentiating this expression with respect to time, we get

$$\frac{dx}{dt}=\frac{1.31}{t},$$

and substituting for x and $\frac{dx}{dt}$ in equation 1, we have

$$\frac{dH}{dt}=\frac{3.93}{r^3t}(r-3\log_{10}t)^2 \tag{3}$$

From this equation the rate at which a particle of radius, r, was being hydrated at any time, t, can be calculated. For instance, at the ages 2, 3, 7, 28, and 180 days, respectively, a 20 micron diameter particle was being used at the rates 16.3, 9.6, 3.1, 0.4, and 0.023 percent per day. By letting $x=10$ in equation 2 we can find the time at which a spherical 20-micron particle would become completely hydrous on the assumption that the same relationship obtained throughout between penetration and age. Doing this, we find t equal to 2,150 days, or 5.9 years. Thus, although this particle is approximately 99 percent hydrated at the end of 1 year, 5 more years are required for the reaction to go to completion if the relation between rate of hydration and time remains the same.

[19] Proc. Am. Soc. Testing Materials **29**, II, 554 (1929).

[20] This cement was chosen because of the simplicity of its equation; the equations for the other cements all contain a constant term.

3. PRACTICAL CONCLUSIONS

A discussion of the effect of fineness of grinding of cement on the properties of concrete, if precedent be followed, perforce should contain some mention of "optimum gradation." This concept of a cement having the best possible gradation for strength purposes, and at the same time one which would yield workable concrete mixes, has been much talked of by past investigators and commentators. It would seem from the results of this investigation that the gradation which would satisfy both of the above requirements really would not be a "gradation" at all in the usual sense of the word, because the particle sizes would have to be restricted to a relatively narrow range.

A cement containing about 70 percent of material between 10 and 20 microns and the remainder less than 10 microns should produce a concrete of almost as high early strength and a higher ultimate strength than any cement graded so as to contain an appreciable amount of material coarser than 20 microns, and it should also yield workable concrete mixes. This cement would have about the same specific surface as blend G and should therefore have about the same 1-day strength, while at the later ages it should develop higher strengths because it would become completely hydrous in a much shorter time. Blend G contained 25 percent of 22–35 micron material and 13 percent of material greater than 35 microns, but on the average the 22–35 fraction only developed about 70 percent at 28 days and 95 percent at 1 year of the strength developed by the 7–22 fraction at the same ages, and the 35–55 fraction was only about 75 percent as strong as the 7–22 at 1 year and less than 50 percent as strong at any of the earlier ages. It is therefore logical to believe that a cement containing only material finer than 20 microns in size would have developed considerably higher strengths than blend G.

In such an "optimum" cement it would appear inadvisable to increase the quantity of 0–7 fraction much above that used in blend G, or 30 percent. Blend H, which contained 47 percent of this fine material, produced cylinders which were honeycombed in some cases and of doubtful compactness in others. Although these cylinders were stronger at early ages, at 1 year they were weaker than the more compact cylinders of blend G. In actual practice it would have been necessary to use a lower cement-water ratio for blend H, and a lower ratio would quite likely have yielded concrete of lower strength. This belief is supported by the results obtained in studying the effect of varying cement-water ratio on the strength of the 0–7 micron fraction. In order to prove that there is a practical limit to specific surface, beyond which no improvement in strength could be attained, it, of course, would be necessary to establish the relations between cement-water ratio and strength for the higher surface blends by actual test.

For the ordinary types of gradation, obtained by commercial grinding, it would seem that there is no such thing as an "optimum." The distribution curves are automatically quite similar, and the most suitable type would be determined by the strength to be required of the concrete. The more finely the cement is ground, within practical limits, the higher will be the early strength, and possibly also the ultimate strength of the concrete. It seems very probable that the hydration process would become arrested, or, at least, very much

retarded, after a short length of time under conditions of practice when the water might escape from the concrete. Under such conditions it would seem desirable to use a cement of high specific surface in order that as much hydration as possible could take place before the reaction became arrested.

The strengths of the concretes made from the blended cements in this investigation were closely related to the specific surface at all ages tested, and it therefore seems that the specific surface is a sufficiently good criterion of strength for practical purposes. If cements having more irregular distribution curves were to be produced, it would probably be advisable to adopt some sort of fineness modulus based upon the amount of hydrous material for different depths of water penetration.

VI. SUMMARY

Five laboratory ground clinkers and one commercial cement have been separated into size fractions, and studies have been made of neat pastes, mortars, and concretes prepared from the fractions as well as from four different blends. The ground clinkers were separated into the five fractions 0–7, 7–22, 22–35, 35–55, and >55 microns. The cement was separated into only four fractions, no separation being made of the material coarser than 35 microns. The four blends ranged in specific surface from about 1,300 to 3,300 cm^2/g. Most of the tests were made both with and without the addition of gypsum.

The fractions of any one cement in most cases showed considerable variations in chemical composition and calculated compound composition. The tricalcium silicate, in general, tends to be more concentrated in the finer sizes, while the higher percentages of dicalcium silicate usually occur in the coarser fractions. The other constituents are about equally distributed.

It was found that all of the fractions, with the exception of the fine 0–7 micron material, were more or less deficient in the power to hold water and that they were lacking in plasticity and good working qualities. These characteristics ranged from the 7–22 micron fraction, which was not vastly different from a whole cement, to the coarsest fraction which behaved very much like a fine sand. The 0–7 micron fraction was very plastic, had a high water-retaining capacity, and was also characterized by an extreme stickiness.

The working qualities of the blends ranged from the coarsest blend, which was possibly somewhat more harsh than the average commercial portland cement, to the highest surface blend which was more plastic and required more water than the ordinary high-early-strength cement. It was found that on the average the amount of water necessary for normal consistency was very nearly a direct function of specific surface. Also, the time of initial set was found to be very closely related to surface.

At one day it was found that strength is directly related to specific surface for both the fractions and the blends. At other ages when strength was plotted against specific surface one line was obtained for the fractions and another for the blends. The strengths of the blends were closely related to specific surface at all ages.

Some good correlations were obtained between strengths and the percentage of hydrous material corresponding to definite depths of water penetration as calculated roughly from the size-distribution

data. The fact that the strengths of the fractions when plotted against the percentage of hydrous material fell on the same lines as those of the blends showed the relationship to be of a more fundamental nature than that existing between specific surface and strength.

Since a much lower cement-water ratio had to be used in molding the strength specimens from the 0–7 micron fraction than in molding those of any of the other fractions or the blends, the strength data obtained for this fine material were not directly comparable with those obtained for the other fractions or the blends. However, the strength of this fraction was calculated from its contribution to the strengths of the blends and these calculated strengths were found to be greater at the early ages than the observed strengths of any of the other fractions and at least as great at the later ages.

Acknowledgment is made to P. H. Bates for valuable suggestions offered during the planning and progress of this investigation. The photomicrographs of the fractions were made by Herbert Insley.

WASHINGTON, February 8, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP778

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

CHEMICAL REACTIONS IN THE LEAD STORAGE BATTERY

By George W. Vinal and D. Norman Craig

ABSTRACT

Although the double-sulphate theory of reactions in the lead storage battery has been generally accepted, its validity has often been challenged because of disagreement between the theory and certain experimental results. One of the chief difficulties in the experimental work lies in determining the amount of electrolyte within the cell, including that portion held in the pores of the plates. The method of mixtures, not previously applied to this problem, has many advantages, and has enabled the authors to determine not only the number of equivalents of acid used per faraday, but also the number of equivalents of water formed. As a result of nine discharges the mean value of the equivalents of acid per faraday was found to be 2.02 ± 0.03 as compared with 2.00 equivalents demanded by the theory. Two equivalents of water were formed under the same conditions. In these experiments the weight of electrolyte was determined at both the beginning and end of discharge.

CONTENTS

	Page
I. Introduction	449
II. Description of the cell	452
III. Manipulation of the cell	453
1. Necessary conditions	453
2. Tests for equalization of acid and the stability of the cell	453
3. Temperature control and precautions against evaporation	455
4. Measurement of coulombs delivered	455
5. Range of current and concentration	455
IV. Method of determining concentration and amount of acid	456
1. Determination of concentration of electrolyte	456
2. Method of calculating weight of electrolyte	457
V. Experimental results	458
1. Direct calculation of acid used and water formed	458
2. Value of the function ϕ	460
VI. Discussion of results	461

I. INTRODUCTION

The "double-sulphate" theory of chemical reactions in the lead storage battery has been accepted by battery engineers generally, but its validity has often been questioned because of disagreement between the theory and certain experimental results. Quantitative proof of the theory involves experimental difficulties that have doubtless been responsible for the variety of results previously obtained. With improved technique for determining the quantity of electrolyte in the cell, a new series of experiments to determine the amount of acid consumed during discharge has been made. The results of these experiments support the double-sulphate theory.

Gladstone and Tribe [1] proposed the double-sulphate theory in 1882 on the basis of their observations that lead sulphate is formed at both positive and negative plates during discharge of the cell and that lead sulphate can be oxidized at one plate and reduced at the other during charge. Their theory is expressed conveniently by the familiar equation

$$PbO_2+2H_2SO_4+Pb\rightleftarrows 2PbSO_4+2H_2O$$

When the cell discharges the reaction proceeds to the right, but this reaction is reversed during charge.

If the equation is true, the passage of one faraday of electricity (96,500 coulombs) in the direction of discharge should result in the consumption of one equivalent each of PbO_2 and Pb and two equivalents of sulphuric acid, while two equivalents each of lead sulphate and water are formed. Numerous experiments to determine the relationship between the quantity of electricity passing through the cell and the materials formed or consumed are recorded in the technical literature.

Gerard [2] suspended the element of a cell from the arm of a balance and determined the changes in weight of the element as it was charged or discharged. He concluded that his results were concordant with the double-sulphate theory. Ayrton, Lamb, and Smith [3] found the quantity of PbO_2 in the positive plates to increase or decrease proportionately to the quantity of electricity passing on charge or discharge, accompanied by equivalent changes in the amount of lead sulphate in both plates. Mugdan [4] concluded from his experiments that the quantity of lead sulphate formed during discharge is essentially that required by the double-sulphate theory.

Many more investigations have been made of the changing density of the electrolyte during charge or discharge. Aron,[5] Crova and Garde,[6] and Kohlrausch and Heim [7] found changes in density of the electrolyte to correspond to their calculations based on the double-sulphate theory. More recently the experiments of Knobel,[8] and Cassel and Tödt [9] have shown that two equivalents of sulphuric acid are consumed per faraday of electricity.

On the other hand, a considerable number of experimenters have found the consumption of sulphuric acid per faraday to be materially less than the two equivalents called for by the double-sulphate theory. Their results vary from 1.2 to 1.8 equivalents of acid per faraday, averaging about 1.5 equivalents. Schenck and Farbaky,[10] Pfaff,[11] Smith,[12] and MacInness, Adler and Joubert [13] are included in this group.

Some writers have expressed the opinion that the active material of the positive plates is not PbO_2 but a higher oxide of lead. Reasons for this belief were based partly on analytical determinations of the

[1] Nature **25**, 221, 461; **26**, 251, 342, 602; **27**, 583 (1882–1883).
[2] Lumière élec. **27**, 387 (1888).
[3] Elektrotech.Z. **12**, 66 (1891).
[4] Z. Elektrochem. **6**, 309 (1899).
[5] Elektrotech.Z. **4**, 58 and 100 (1883).
[6] Lumière élec. **16**, 471; **17**, 219 (1885).
[7] Elektrotech.Z. **10**, 327 (1889).
[8] Trans.Am.Electrochem. Soc. **43**, 99 (1923).
[9] Z.angew. Chem. **36**, 227 (1923).
[10] Dinglers polytech. J. **257**, 357 (1885).
[11] Centr. Accumulatoren **2**, 73 and 173 (1901).
[12] Mentioned in reference of footnote 13.
[13] Trans.Am.Electrochem.Soc. **37**, 641 (1920).

material and partly on values less than two for the equivalents of acid used per faraday. Drzewiecki,[14] Féry,[15] and Bary [16] have discussed the so-called "higher oxides." Féry proposed a theory for the reaction involving a higher oxide of lead at the positive plate and the formation of a subsulphate of lead at the negative plate. Féry's reaction would require the consumption of only one equivalent of acid per faraday of electricity. Determinations mentioned above, averaging about 1.5 equivalents, are therefore intermediate between requirements of the two theories and support neither.

MacInness, Adler and Joubert [17] showed that the active material of freshly charged positive plates had the same composition and electrical potential as lead dioxide prepared chemically or by anodic deposition on platinum. Their results make any reaction based on a higher oxide of lead seem very questionable.

The formation of a basic sulphate during discharge has been suggested in explanation of less than two equivalents of acid being used per faraday. Such a suggestion is apparently favored by Knobel [18] as an explanation of departures which he observed at high rates of discharge. Riesenfeld and Sass,[19] however, consider a basic lead sulphate as the normal product of discharge at the positive plate.

Within recent years the X-ray spectrograph has been used to identify chemical compounds in the storage battery. It would seem that this method should provide an unequivocal answer to the problem, but differences in opinion have arisen. Mazza [20] studied the compounds of the reaction by the use of X-rays and found battery plates in the charged condition to consist of lead dioxide (positives) and lead (negatives). In the discharged condition lead sulphate was found in both positive and negative plates, in addition to the original materials. Barrett [21] confirmed the conclusions of Mazza. Riesenfeld and Sass [22] on the other hand have found evidence that during discharge basic lead sulphate is formed at the positive plates and that this changes on standing to the neutral sulphate. In support of their theory, they cite experiments in which the acid consumption per faraday was found to be materially less than two equivalents.

Recently, Kameyama [23] has refuted the argument of Riesenfeld and Sass on thermodynamic grounds.

The work of others might be cited in support of or in opposition to the double-sulphate theory, but the conflict of opinion is clearly apparent. The question at the present time hinges on the correct determination of the amount of acid used per faraday. We believe the varying results obtained in the past have been due chiefly to the difficulty in determining the amount of acid in the cell. The free electrolyte in the cell can be measured easily, but to this must be added the electrolyte in the pores of the plates and separators. Porosity of the plates changes during discharge, making corrections for the amount of electrolyte held in the pores uncertain. If the plates are washed or dried before placing them in a measured quantity of electrolyte, their condition is not normal.

[14] Bul.soc.int.élec. **6**, 414 (1889).
[15] Lumière élec. **34**, 305 (1916); Rev.gén.élec. **1**, 10 (1917); **19**, 296 (1926).
[16] Rev.gén.élec. **6**, 195 (1919).
[17] See footnote 13.
[18] Trans.Am.Electrochem.Soc. **43**, 99 (1923).
[19] Z. Elektrochem. **39**, 219 (1933).
[20] Atti.accad.Lincei [6] **4**, 215; **5**, 117, 688 (1927).
[21] Ind.Eng.Chem. **25**, 297 (1933).
[22] See footnote 19.
[23] J.Electrochem.Assn. (Japan) **1**, 3 (1933).

We have used the "method of mixtures" for determining the amount of acid in the cell, both at the beginning and end of discharge. Our cell has not been dismantled at any time for the purpose of measuring the acid. In principle, it is based on the fact that if to a solution of known concentration but unknown weight a carefully measured portion of water or another solution differing in concentration be added, and the concentration again determined, the weight of both the original and final solution can be calculated. This method has not been used previously in this particular problem so far as we are aware. It has many advantages for the purpose and has enabled us to determine not only the number of equivalents of acid used per faraday, but also the number of equivalents of water formed.

II. DESCRIPTION OF THE CELL

The cell consisted of 11 pasted plates, 5 positives and 6 negatives, contained in a rectangular glass jar having a capacity of about one-half liter. Each plate was 9 by 2.5 by 0.3 cm. The grids were castings of pure lead having a volume 1.8 cm^3 and providing space for 5.7 cm^3 of active material. Each grid was provided with a long stem or terminal post, which was burned to the grid, using pure lead. The plates, which were made in the laboratory, were pasted with lead oxide mixed with dilute sulphuric acid. To the paste for negative plates, ¼ percent of lampblack was added as an expander. The procedure for pasting the plates was similar to that previously described.[24]

The plates, after being pasted, were pickled in sulphuric acid of specific gravity 1.150 for 20 hours. They were formed at 0.4 ampere in a small tank containing sulphuric acid, initially 1.150 specific gravity. At the conclusion of formation the voltage across the cell was 2.63 volts, and cadmium voltages were +2.42 and −0.24 for the positive and negative groups, respectively.

After formation the plates were cycled ten times in sulphuric acid of specific gravity 1.250. Charging was done at 0.5 to 0.75 ampere and discharging at 1.5 ampere. During the preliminary cycling the capacity of the cell increased and the cadmium voltage of the negative plates changed to −0.28. This rather large numerical value is characteristic of plates not containing antimony.

When the plates were assembled in the cell they were spaced approximately 0.4 cm apart. The stems of individual plates were brought through holes in a hard-rubber cover and extended considerably above the cover. Glass tubes 6 to 7 cm long and extending above and below the cover were placed over each stem to provide additional insulation between adjacent terminals of opposite polarity. These glass tubes were supported by short sections of rubber tubing, which served also to seal the upper ends of the glass tubes.

Slotted-rubber separators and glass rods were placed between adjacent plates of opposite polarity. Wood separators were not used as we desired to have free circulation of the electrolyte.

Above the tops of the plates a free space of about 200 cm^3 provided for the addition of weighed amounts of water or relatively concentrated solutions of sulphuric acid as a means of changing the density of

[24] Vinal, Craig and Snyder, BS J.Research **10**, 798 (1933) RP567.

solution within the cell. Vent holes in the cover, normally closed with cork stoppers, provided for adding or withdrawing samples of electrolyte from the cell and also for stirring the electrolyte by means of an air jet before making titrations or density determinations.

III. MANIPULATION OF THE CELL

1. NECESSARY CONDITIONS

The first requisite for the successful operation of the cell in determining the relation of electrochemical products to the quantity of electricity discharged is that the cell shall be in normal operating condition. That is, the cell must be operating on a program of charges and discharges without interruptions, such as removing the plates for determination of their weight or porosity. Any unusual operation on the cell before beginning the experiment leaves a doubt whether it is in normal condition.

The second requirement is that means must be provided to determine with high precision the weight and concentration of the electrolyte in the cell before and after each discharge.

The third requirement is that the cell shall be as free as possible from local action.

The fourth requirement calls for high accuracy in electrical measurements of the coulombs discharged by the cell and of its electromotive force before and after each discharge as a test of the stability of the cell. These requirements have been met as described in the following paragraphs.

We have prepared our cell by cycling it in the usual way up to the time for making the experiment and then determined the amount of electrolyte within the cell by observing the change in concentration when a carefully weighed portion of distilled water or sulphuric-acid solution is added. Such a change in equilibrium is essentially the same as occurs in the normal operation of the cell and it interferes in no way with the condition of the plates.

2. TESTS FOR EQUALIZATION OF ACID AND THE STABILITY OF THE CELL

After each addition of water or solution, it is necessary that the electrolyte be completely equalized throughout the vessel and the pores of the plates. We have two tests for determining when this is accomplished.

Since the electromotive force (emf) of the cell is dependent on the concentration of the electrolyte, constancy of emf is an indication that the electrolyte is homogeneous throughout the cell. To avoid the difficulty which often arises in measuring the emf of a storage cell because its emf exceeds the range of the ordinary potentiometer, we opposed the emf of the storage cell to the emf of a standard cell, and measured the difference directly on a potentiometer. The emf of the standard cell was determined daily in terms of the Bureau's primary standard of emf. This value added to the observed difference in emf between the cells gave the emf of the storage cell with high precision.

The rapidity with which equalization is accomplished and the stability of the cell thereafter is shown by the results in tables 1 and 2. Table 1 gives measurements of emf after the completion of the dis-

charge of April 13. This table shows that the emf of the cell became practically constant in 2 hours. When the electrolyte was diluted 19 hours after concluding the discharge for the purpose of determining the amount of electrolyte in the cell, a period of about 2 hours was required before the emf again became constant to 0.3 millivolt. The constancy of emf when equalization is established shows the stability of the cell and its freedom from local action, electrical leakage, etc.

TABLE 1.—*Measurements of electromotive force at 24° C*

Experiment of April 13, 1934

(Time is reckoned from termination of the discharge)

Time		Emf	Remarks
Hours	*Minutes*	*Volts*	
0	0		Discharge stopped.
	10	1.977	Electrolyte stirred at 0 hr, 5 min.
1	20	2.0334	
1	40	2.0348	Electrolyte stirred at 1 hr, 25 min.
2	20	2.0346	
6	30	2.0349	Electrolyte stirred at 6 hr, 35 min.
17	30	2.0352	Electrolyte stirred at 17 hr, 35 min.
18	30	2.0349	
19	0		Electrolyte diluted and stirred.
19	30	1.9897	Electrolyte stirred at 19 hr, 35 min.
19	40	1.9879	
20	35	1.9811	Electrolyte stirred at 20 hr, 40 min.
21	30	1.9789	Electrolyte stirred at 21 hr, 35 min.
21	45	1.9798	
29	0	1.9794	Electrolyte stirred at 29 hr, 05 min.
30	0	1.9794	
42	0	1.9795	
90	0	1.9795	
114	0	1.9796	

Table 2 shows the results of repeated measurements of concentration of the solutions following the discharge of November 30. As in the preceding table, constancy is attained by allowing the cell to stand. The observed change in concentration which occurred between 3 hours 50 minutes and 13 hours 35 minutes after stopping the discharge amounted only to 5 parts in 1,000 of the total change resulting from the discharge of the cell. The electrolyte was then concentrated for the purpose of determining the quantity of electrolyte. Between 27 and 50 hours the change was within the experimental error.

TABLE 2.—*Measurements of concentration of electrolyte*

Experiment of November 30, 1934

(Time is reckoned from termination of the discharge)

Time		Concentration	Remarks
Hours	*Minutes*	*Percent*	
0	0		Discharge stopped.
3	50	23.534	Stirred at 3 hr, 20 min.
11	35	23.594	Stirred at 11 hr, 20 min.
12	10	23.582	
12	35	23.588	Stirred at 12 hr, 20 min.
13	35	23.579	
14	20		Concentrated acid added and stirred.
27	20	*34.153	Stirred at 26 hr, 50 min.
50	50	*34.164	Stirred at 50 hr, 20 min.

* Average of three determinations.

3. TEMPERATURE CONTROL AND PRECAUTIONS AGAINST EVAPORATION

The earlier experiments were made while the storage cell was immersed in a thermostatically controlled oil bath. The object in controlling the temperature was to permit making precise measurements of electromotive force before and after discharge as a test of complete equalization of electrolyte throughout the cell. Although the cell was closed by a cover, evaporation was not completely prevented.

Experiment 8, which was made in two parts with great care, showed conclusively that evaporation was appreciable. Frequent weighings of the cell were made on a balance sensitive to 0.1 gram. The progressive loss in weight of the cell accompanied by a progressive increase in density of electrolyte while the cell was on open circuit indicated that additional precautions against evaporation were necessary.

The loss of water by evaporation depends on temperature and atmospheric conditions as well as on concentration. No corrections for this loss during the earlier experiments could be made. The amount probably varied from 0.5 to 1.0 gram or even more per day. This is a relatively large percentage of the total amount of water formed during discharge.

In all the later experiments, therefore, the use of the thermostatically-controlled oil bath was abandoned and the cell was kept under a sealed bell jar, except when the discharge was actually in progress. At such times it was in a covered glass vessel. Repeated weighings of the cell showed that its weight was much more constant under these conditions. It then became possible to determine with accuracy the water formed during discharge as well as the acid consumed.

4. MEASUREMENT OF COULOMBS DELIVERED

In some of the earlier measurements the current was measured by a calibrated ammeter, but in the later experiments we used a precision 1/10-ohm shunt, measuring the fall in potential across its terminals on a potentiometer. Readings were taken at frequent intervals and the time integral of the current obtained. Time was measured by reference to the Bureau's standard clocks. In all experiments an ampere-hour meter was included in the circuit as a check, but we have preferred to base the coulombs delivered by the cell on the more accurate measurements of current and time.

5. RANGE OF CURRENT AND CONCENTRATION

The electric current and concentration of electrolyte have been varied purposely from one experiment to another in order that the results of the experiments may not be limited to any particular conditions. The largest current used in any of the experiments was 1.8 amperes and the smallest was 0.6 ampere. These currents correspond approximately to the 5-hour and 20-hour rates for the cell. The highest initial concentration of the electrolyte was 42 percent and the lowest 21 percent. At the end of the discharge the highest concentration was 38 percent and the lowest about 9 percent. Experiment 8 was made in two parts and the equivalents of acid

used per faraday for each part were compared. Notwithstanding these variations in current, concentration, or part of the discharge, no significant differences in the equivalents of acid used per faraday were found.

IV. METHOD OF DETERMINING CONCENTRATION AND AMOUNT OF ACID

1. DETERMINATION OF CONCENTRATION OF ELECTROLYTE

Three methods were used for measuring the concentration of the acid. In the first two experiments the samples of acid withdrawn from the cell were titrated with CO_2-free sodium-hydroxide solution. The sodium-hydroxide solution, approximately 0.2 N, was standardized with acid potassium phthalate.

In experiments 3 to 5, the accuracy of the acid determinations was improved by making all titrations by weight. To the weighed sample to be titrated, a weighed amount of 0.2 N sodium hydroxide was added, stopping short, however, of the final end point, which was then determined volumetrically by using a solution of 0.02 N sodium hydroxide. The latter was freshly prepared and standardized before each experiment. All titrations were done in triplicate, the individual measurements agreeing to 0.01 percent of sulphuric acid.

For experiments 6 to 12, we used a third method for determining the amount of sulphuric acid in the electrolyte. The density $\frac{26.5^\circ\ C}{4^\circ\ C}$ was determined with a pycnometer immersed in a thermostatically-controlled water bath. Density determinations were then calculated to percentages of sulphuric acid by using data in the International Critical Tables. In some experiments, interpolation of data in the Critical Tables was carried to five figures. This was done in those cases where the density was very nearly the same after the final concentration as it was at the beginning of the discharge.

The pycnometer was a bulb of Pyrex glass of about 15-ml capacity and provided with a graduated capillary stem. It was filled and emptied by a capillary glass tube. Repeated measurements were made, the agreement being indicated by the following group of density measurements, which were part of the experiment of November 30: 1.16308, 1.16299, 1.16304, 1.16297, giving an average value 1.16302. The maximum difference of a single observation from the mean is 5 parts in 100,000.

Accuracy in determining the concentration of acid in the solutions is important, because the determination of the weight of electrolyte in the cell depends on the difference in concentration produced when a weighed portion of water or sulphuric-acid solution is added to the electrolyte in the cell. The factor which cannot readily be controlled is the difference in solubility of lead sulphate in sulphuric-acid solutions of various concentrations. For the extreme range in concentrations which we have used, the solubility of lead sulphate as given by Dolezalek [25] ranges from 0.01 mg-mol of $PbSO_4$ in 1 gram-mol of sulphuric acid to 0.07 mg-mol of $PbSO_4$ in 6 gram-mols of sulphuric acid per liter. In other words, the lead sulphate in solution varied from 3 to 16 parts per million. We have not attempted to make correction for this dissolved lead sulphate.

[25] Theory of the Lead Accumulator, page 145.

2. METHOD OF CALCULATING WEIGHT OF ELECTROLYTE

When a weighed portion of water or of sulphuric acid of specified concentration is added to another portion of sulphuric acid of known concentration, but unknown weight, it is possible to determine both the weight of the latter and of the mixture on the basis of the concentration of the resulting solution. Thus determinations of the weight of electrolyte in the cell at the beginning and end of a discharge have been made for all experiments except 1 and 7. For these the respective weights of electrolyte have been determined only at the end of the experiments. Particular care has been taken to equalize the electrolyte in all portions of the cell (see page 453) before attempting to determine the weight of electrolyte.

The method of calculating the weight of electrolyte by mixing two portions of unlike concentration is shown in the following example In all cases the mixtures were made within the cell. Samples removed for titration were carefully weighed and allowance made for them.

The following data apply to experiment 11 of December 7: (concentrations are expressed as the weight fraction)—

Initial concentration of electrolyte 0. 22783
Acid added { concentration 0. 59820
weight ..... 117. 684 g
Concentration of resulting mixture 0. 33447
Let y=weight of electrolyte after mixing

$$\frac{0.33447y-(0.59820\times 117.684)}{y-117.684}=0.22783$$

whence ..... y=408. 73 g
Deduct for sample removed ..... 60. 66 g

Net weight of electrolyte at start of discharge ..... 348. 07 g

A similar method was used to determine the weight of electrolyte at the end of discharge. The percentage strength and weight of electrolyte for each experiment are given in table 3.

TABLE 3.—*Amounts of sulphuric acid consumed and water formed in discharging a lead storage battery*

Experiment	Date	Discharge data		Percentage of H_2SO_4 (by weight)		Weight of solution		Acid used	Water formed
		Time	Coulombs	Start	Finish	Start	Finish		
	1934	*Hours*				*Grams*	*Grams*	*Grams*	*Grams*
1	Mar. 9	10. 42	45252	35. 53	24. 82		311. 2		
2	Mar. 20	7. 81	34992	36. 60	29. 17	358. 77	330. 60	34. 87	6. 70
3	Mar. 27	8. 00	35833	28. 061	18. 933	341. 78	307. 65	37. 66	3. 53
4	Apr. 6	8. 83	39116	30. 885	21. 684	358. 71	324. 73	40. 38	6. 40
5	Apr. 13	4. 83	31232	32. 518	25. 607	364. 20	337. 88	31. 91	5. 59
6	Oct. 5	10. 60	42088	28. 21	17. 89	355. 33	317. 20	43. 49	5. 36
7	Oct. 17	5. 84	23130	42. 714	38. 246		345. 92		
8a	Oct. 31	5. 03	19786	20. 951	15. 850	347. 73			
8b		5. 80	22316	15. 850	8. 898		[a] 284. 98		
9	Nov. 23	5. 75	22638	41. 24	36. 72	360. 85	340. 28	23. 86	3. 29
10	Nov. 30	19. 87	44173	33. 948	23. 584	351. 22	315. 14	44. 91	8. 83
11	Dec. 7	6. 73	31237	33. 447	26. 276	348. 07	323. 13	31. 51	6. 57
12	Dec. 27	13. 42	38152	31. 141	22. 298	359. 09	326. 87	38. 94	6. 72

[a] Between the two discharges 18.62 grams of electrolyte were removed for density determinations.

V. EXPERIMENTAL RESULTS

1. DIRECT CALCULATION OF ACID USED AND WATER FORMED

In the course of most of our experiments we determined the weight and percentage strength of electrolyte at the beginning and end of discharge. Sufficient data were provided thereby to calculate directly the amount of acid consumed and water formed as a result of the reaction. No assumptions regarding the correctness or applicability of any theory of chemical reactions in the battery are necessary, therefore, in computing the number of equivalents of acid and water taking part in the reaction. We know of no previous attempt to determine the amount of water formed by the process of discharge, nor of calculations of the acid consumed, which are thus independent of theoretical assumptions.

Nine of the twelve experiments reported in table 3 give directly the amounts of acid and water taking part in the reaction. Of the remaining three experiments, the first and seventh lack the initial weight of electrolyte and the eighth was subject to error in determining the water because of evaporation. These three experiments will be discussed later.

Table 4 gives the results of nine experiments in terms of the equivalents of acid consumed and water formed per faraday. The number of equivalents of H_2SO_4 consumed per faraday is equal to

$$\frac{F}{C}\frac{(pw-qw')}{49.04},$$

and the number of equivalents of H_2O formed per faraday is equal to

$$\frac{F}{C}\frac{(pw-qw')-(w-w')}{9.01}.$$

In these expressions

w = weight of electrolyte at beginning of discharge
w' = weight of electrolyte at end of discharge
p = weight fraction of sulphuric acid at beginning of discharge
q = weight fraction of sulphuric acid at end of discharge
c = coulombs of electricity discharged
F = value of faraday = 96500 coulombs
Equivalent weight of sulphuric acid = 49.04 g
Equivalent weight of water = 9.01 g

It can be seen that the expressions for the equivalents of H_2SO_4 and H_2O per faraday involve no assumptions regarding the reaction and that each of the unknown quantities can be determined experimentally. The average result of the equivalents of acid used per faraday is 2.02 ± 0.03, whether all the experiments are included in the average or only the last four. The water determinations show more variation as would be expected. The mean of the last four experiments, in which evaporation was avoided, is 1.96 ± 0.19 equivalents per faraday.

Direct determinations of the acid used and water formed afford a severe test of the accuracy of the work. The average amount of electrolyte in the cell was about 335 grams, but the actual change in weight of the electrolyte from the beginning to end of a discharge

averaged only 35 grams. If an error as large as 1 gram were made in determining the total weight of electrolyte, the percentage error would be only 0.3 percent, but in calculations based on the difference of the initial and final weights it would be 3 percent, or an error ten times as great. The water formed is a still smaller part of the change in weight of electrolyte and the supposed error of 1 gram in weight of the whole solution becomes about 15 percent of the water determination. It is apparent, therefore, that the weight of electrolyte must be determined very accurately if the direct calculations of water formed and acid used are to be sufficiently precise to prove any particular theory.

TABLE 4.—*Equivalents of acid consumed and water formed per faraday during discharge of the lead storage battery*

Experiment	Equivalents per faraday	
	H_2SO_4	H_2O
2	1.96	2.05
3	2.07	1.06
4	2.03	1.75
5	2.01	1.92
6	2.03	1.36
9	2.07	1.56
10	2.00	2.14
11	1.99	2.25
12	2.01	1.89
Mean of all	2.02	1.78
Average deviation	± 0.03	± 0.30
Mean of last four	2.02	1.96
Average deviation	± 0.03	± 0.19

In experiments 3 and 6 the observed amount of water was proportionally less than that of several other experiments. In attempting to find why this should be, experiment eight was made with great care and an unusually long time was required for many repetitions of the density measurements. The results obtained by calculating the water formed in this experiment were even worse than before. The cell was weighed periodically and found to be losing weight by roughly 0.5 gram per day, while the density of the electrolyte was gradually increasing. Weighings were made on a balance sensitive to 0.1 gram. All the evidence indicated evaporation to be the cause of the discrepancy in amount of water.

Evaporation of water from the electrolyte was doubtless a source of error in several of the earlier experiments, particularly 3 and 6, for which the percentage strength of the acid was low. We have no way of correcting for loss of water in these experiments, but beginning with the ninth experiment added precautions were taken to prevent evaporation. The weight of the cell in these last experiments remained nearly constant. The results of water determinations of the last four experiments are regarded, therefore, as more reliable than those which preceded.

Clearly the results in table 4 show that two equivalents of acid are consumed per faraday and that two equivalents of water are formed simultaneously. Comparing these figures with the requirements of the several theories mentioned on page 451, it is found that they

satisfy exactly the requirements of the double-sulphate theory, but fail to support any of the other theories.

Previous calculations of the equivalents of acid used per faraday have been based on a single determination of the weight of electrolyte, usually at the beginning of discharge. Such calculations assumed that an equal number of equivalents of acid and water were involved in the reaction. This had not been proved, but the assumption now appears to have been entirely justified.

We are now in a position to calculate the results of all of our experiments, including the three which were omitted from table 4. By doing this our results are presented in a manner analogous to that of previous investigators and accidental errors in determining the weight of solution become far less important than when we are dealing with the difference in weight at the beginning and end of a discharge.

2. VALUE OF THE FUNCTION ϕ

The equivalents of sulphuric acid which were consumed per faraday of electricity, ϕ,[26] were calculated by the method used by some previous experimenters, that is from the change in concentration of the electrolyte during the experiment and the known weight of the electrolyte at either the beginning or end of discharge. In those of our experiments for which we determined the weight of electrolyte both at the beginning and end of discharge, it is possible to compute two independent values for ϕ, table 5. One computation serves as a check on the other, but they are independent inasmuch as each is based on independent determinations of the weight of electrolyte.

TABLE 5.—*Equivalents of sulphuric acid consumed per faraday in discharging a lead storage battery*

Experiment	Value of ϕ		Method for determining acid concentration
	Equation 1	Equation 2	
1		2.04	Titration by volume.
2	1.97	1.97	Do.
3	2.026	2.000	Titration by weight.
4	2.017	2.010	Do.
5	2.005	2.003	Do.
6	2.008	1.988	Density.
7		2.019	Do.
8a	2.026		Do.
8b		2.007	Do.
9	2.025	2.015	Do.
10	2.008	2.013	Do.
11	2.001	2.008	Do.
12	2.002	1.999	Do.
Mean	2.009	2.006	
Mean of all	2.007		
Average deviation from mean	±0.011.		

Using the weight of electrolyte determined at the beginning of discharge

$$\phi=\frac{wF(p-q)}{c\,(49.04-40.03q)}=\frac{2410.7\,w\,(p-q)}{c\,(1.2251-q)} \tag{1}$$

[26] Reference footnote 8, Trans. Am. Electrochem. Soc. 43, 99 (1923).

Similarly, using weight of electrolyte determined at end of discharge

$$\phi=\frac{w' F (p-q)}{c (49.04-40.03 p)}=\frac{2410.7 w' (p-q)}{c (1.2251-p)} \quad (2)$$

Applying the formulas 1 and 2 to the data of experiment 11 of December 7, as given in table 3, ϕ is calculated to be

By formula 1 ..... $\phi=2.001$
By formula 2 ..... $\phi=2.008$
Using formula 1 based on the weight of electrolyte at the beginning of each discharge, the average result for all the experiments is ..... $\phi=2.009$
Probable error of mean ..... $\pm.003$
Similarly, using formula 2 based on the weight of electrolyte at the end of each discharge, the average result for all the experiments is ..... $\phi=2.006$
Probable error of mean ..... $\pm.003$

The two values for ϕ agree, therefore, within probable errors.

The average of 22 determinations of ϕ is ..... $\phi=2.007$
Average deviation of a single observation ..... $\pm.011$

This value for ϕ agrees closely with the theoretical value, 2, given by the equation representing the double-sulphate theory.

VI. DISCUSSION OF RESULTS

Throughout the experiments the cell was unusually stable. Repeated measurements of its electromotive force and of the concentration of its electrolyte have shown constant values after sufficient time had elapsed for equalization of the acid. During the 6 months from April 13 to October 5 when experiments were not in progress, the cell stood in a partially charged condition without harmful sulphation occurring or visible liberation of gas from the negative plates. We believe this stability was the result of constructing the cell with pure-lead grids, the use of reagent grade of sulphuric acid for the electrolyte, and the insulation of the terminal of each plate with a long glass tube. Such a cell may be expected to hold its charge for 6 months or a year.

Although pure sulphuric acid was used for the electrolyte, small amounts of lead sulphate dissolved in it as the cell was worked. The amount varied with the concentration of the acid, but in any case probably did not exceed 0.1 mg-mol per liter. We were justified, therefore, in basing calculations of percentage strength on data applying to pure sulphuric-acid solutions. We do not have sufficient data on the variation of the solubility of lead sulphate with acid concentration to warrant applying a correction for it.

Tables 4 and 5 show that most of our determinations of the equivalents of acid used per faraday are slightly above the theoretical value, 2, based on the double-sulphate theory. Several possible causes for this may be mentioned although it is not certain that any one of them was responsible. First, the unequal solubility of lead sulphate in the stronger solutions at the beginning of discharge as compared with the more dilute solutions at the end may have produced a slight effect. Second, an unobserved precipitate of lead sulphate may have

introduced a small error in the density determinations. We guarded against such a possibility by repeating density measurements at intervals of one-half to one hour after stirring the electrolyte. If a precipitate was settling out, concordant results could not have been obtained.

Riesenfeld and Sass [27] in commenting on the work of Cassel and Tödt [28] emphasized the fact that the latter obtained two equivalents of acid used per faraday only after the lapse of considerable time following each discharge. Determinations made shortly after completion of discharge, on the other hand, were less than two by significant amounts. Cassel and Tödt have attributed low values to incomplete equalization of electrolyte, but Riesenfeld and Sass believe that the low values cannot be accounted for in such a manner. The latter think that a chemical reaction occurs during the period of standing, by which basic lead sulphate is transformed to neutral sulphate. We have examined the records of our experiments in which samples of electrolyte were taken soon after the termination of discharge and have computed values of ϕ, which are given in table 6. In all cases, values approximating two were obtained, including the measurement made only 15 minutes after the conclusion of the discharge when equalization of the acid in the pores of the plate was probably incomplete. Our work in this respect does not confirm the hypothesis of Riesenfeld and Sass.

TABLE 6.—*Effect of time of sampling on values calculated for* ϕ

Experiment	Time of sampling after discharge		Value of ϕ	Remarks
	Hours	*Minutes*		
8	0	15	1.976	
	3	30	2.010	
	15	0	2.026	Steady value.
9	1	45	2.024	
	4	45	2.022	
	19	0	2.024	Steady value.
10	4	0	2.016	
	13	0	2.008	Steady value.

The results of our work are entirely consistent with the double-sulphate theory and we have shown that 2.02 ± 0.03 equivalents of acid are used and 1.96 ± 0.19 equivalents of water formed by the passage of one faraday of electricity through the cell in the direction of discharge. We have found no evidence of the formation of basic sulphate or any spontaneous change occurring in the cell when on open circuit after discharge.

WASHINGTON, January 19, 1935.

[27] Z. Elektrochem. **39**, 219 (1933).
[28] Z. angew. Chem. **36**, 227 (1923).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP779

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

RELATION OF INK TO THE PRESERVATION OF WRITTEN RECORDS

By Elmer W. Zimmerman, Charles G. Weber, and Arthur E. Kimberly [1]

ABSTRACT

The life of written records depends on the stability of both the paper and the ink. Investigation of the comparative resistance of inked and uninked specimens to the effects of an accelerated-aging test, consisting in heating the samples 72 hours at 100° C, revealed that the rate of deterioration of writing papers was increased by the common type of writing inks. The effect on papers suitable for permanent records, which deteriorated very little when uninked, was more apparent than on papers of lower grade. An ink made with ammonium ammoniumoxyferrigallate was found to have a minimum of deleterious effect.

CONTENTS

	Page
I. Introduction	463
II. Inks and papers studied	464
III. Procedure	465
IV. Results of tests	465
1. Comparative qualities of the inks tested	465
2. Relative effects of inks on different papers	466
3. Influence of ink on acidity of paper	467
4. Reproducibility of results	467
V. Summary and conclusions	468

I. INTRODUCTION

Many records are still preserved in manuscript form, the permanence of which depends upon the type of paper and ink used. A study of writing papers at the National Bureau of Standards has revealed much information relative to the influence of the properties of paper and the conditions of storage on the lasting quality of record papers.[2] The work of previous investigators [3] shows that some inks have a deteriorative effect on paper. The published results are contradictory with respect to the effects of the separate components of ink on paper, and modern types of domestic record papers were not included in the experiments. The work here described was undertaken to obtain information regarding the effect of writing inks and their components on domestic papers.

[1] Formerly Research Associate at the National Bureau of Standards for the National Research Council.
[2] A. E. Kimberly and B. W. Scribner, Misc.Pub.BS M144 (1934).
[3] C. Wurster, Ber. Deut. Chem. Ges. **10,** 1794 (1877).
O. Schluttig, and G. S. Neumann, Die Eisengallustinten, V. Zahn und Jaensch (Dresden, 1890).
P. Ehrle, Zentr. Bibliothekwesen. **15,** (1898)
Posse. Apollo Press (Dresden, 1899).
O. Winkler, Z.angew, Chem. **16,** 27 (1903).
A. J. J. Vandervelde, Rev. Bibliothéques Arch. Belgique **4,** 77 (1906).
W. Haerting, Kolloid-Z. **25,** 74 (1919).
W. Herzberg, Papierprüfung, p. 67 (Berlin, 1866).
W. Herzberg, Mitt. Materialprüfungsamt, Berlin-Dahlem, **40,** 90 (1922).
W. Herzberg, Paper Makers' Monthly J. **61,** 236 (1923).
W. Herzberg, Wochbl. Papier-Fabr. **55,** 335 (1924); Chem. Abst. **18,** 1750 (1924).

II. INKS AND PAPERS STUDIED

Three inks were first prepared in the laboratory, using the specification for government standard writing ink [4] as a guide. The first was made according to the specification. The second was a duplicate of the first, except that a chemically equivalent amount of sulphuric acid was substituted for the hydrochloric acid, and the third was like the second with one percent of gum arabic added. These inks are numbered 1, 2, and 3 respectively in table 1. Seven solutions, listed in table 2, were also prepared, each of which contained a different component or a combination of components of the concentration used in ink number 1. With the information on the action of these inks and the solutions of their ingredients as a guide, nine additional writing inks (numbered 4 to 12 in table 1) were prepared for testing. Materials of the ordinary reagent quality were used for all of the ingredients except the ferrous sulphate, which was purified by precipitation with alcohol.[5]

TABLE 1.—*Test data on writing inks*

Paper no. 7

Formula number	Constituents of inks, grams per liter of water															Corrosion—mg iron dissolved in 2 days by 25 ml of ink	Stability in approximate days for sediment to form in test	Writing quality and appearance	Retention of folding endurance after heating, in percentage of initial endurance
	Tannic acid	Gallic acid	Ferrous sulphate, $FeSO_4.7H_2O$	Ferric chloride, $FeCl_3.6H_2O$	Ammonia, NH_3	Gum arabic	Hydrochloric acid as HCl	Sulphuric acid	Oxalic acid	Sodium oxalate	Tartaric acid	Phenol	Prussian blue	Ammonium ammoniumoxyferrigallate	Soluble blue				
1	11.7	3.8	15				1.25					1			3.5	36	14	Good	50
2	11.7	3.8	15					1.7				1			3.5	36	14	do	54
3	11.7	3.8	15			10		1.7				1			3.5	34	28	do	52
4													15			4	[a] 30+	do	58
5	11.7	3.8	15			10	1.25									33		Poor	50
6	8.4	7.7		15						2.3					3.5	2	14	Good	33
7	8.4	7.7		15					21.6						3.5	4	14	do	13
8		18		15		10									3.5	54	28	do	20
9		10	15			10					2.7				3.5	47	40	do	51
10		16.2		23.1	7.3							1			3.5	12	25	do	17
11														60		19	50+	do	57
12														20		18	50+	do	68
																			[b] 72

[a] + indicates test was stopped before a sediment appeared. [b] Uninked paper.

TABLE 2.—*The influence of ink constituents on the deterioration of paper no. 7 and on the corrosion of steel pens*

Solution	Ink constituents in solution	Corrosion of steel, g of iron dissolved by 25 ml of ink	Retention of folding endurance after heating, in percentage of initial endurance
A	Tannic acid, gallic acid, $FeSO_4$	.008	57
B	Tannic acid, gallic acid	.008	73
C	Tannic acid, gallic acid, HCl	.034	70
D	HCl	.029	60
E	HCl, $FeSO_4$	.028	59
F	HCl, $FeSO_4$, tannic acid, gallic acid	.035	54
G	$FeSO_4$	.004	60
			[a] 73

[a] Untreated paper.

[4] Federal Specification TT-I-563, Ink; Writing.

[5] E. Thorpe, Dictionary of Applied Chemistry, III, 861 (Longmans, Green, and Co., London, 1922).

Seven writing papers, varying as to fiber composition and sizing materials, were selected for use in the tests. These papers are described in table 3.

III. PROCEDURE

In order to determine the effect of the writing inks on the deterioration of paper, inked and uninked specimens of the papers were subjected to an accelerated-aging test [6, 7] that has been employed by this Bureau for estimating the relative permanence of papers.[8]

The inked specimens were prepared by drawing parallel lines approximately 0.02 inch wide, spaced 0.036 inch apart, across one-half of each sheet of paper. The lines on half of the sheets were parallel to the machine direction of the paper, and on the others were at right angles to the machine direction. The sheets were conditioned two weeks in an atmosphere of 65 percent relative humidity at 70° F and then aged at 100° C for 72 hours. The folding endurance of the samples was determined on an MIT folding-endurance tester.[9] The results of 20 tests, 10 made parallel to the machine direction and 10 made at right angles to the machine direction of the paper, were averaged to give each of the figures reported in the tables. In each case the folds were made at right angles to the ink lines. The relative stability of the inked and uninked specimens, as shown by the decrease in the retention of folding endurance after the accelerated-aging test, was considered indicative of the deteriorative effect of the ink on the paper. Inked and uninked specimens were conditioned and tested simultaneously.

All of the papers were tested with inks 1, 2, and 3 in order to find the influence of the paper on the ink, and all the inks were tested on one paper to compare the relative effect of the different inks. The inks were also tested for sediment and corrosion by the methods given in the specification for writing ink [10], and the writing quality was observed.

IV. RESULTS OF TESTS

1. COMPARATIVE QUALITIES OF THE INKS TESTED

The standard writing inks were all found to be very harmful to the paper. The effects were so serious that further investigation was confined to different types of inks in an effort to find one less harmful to paper. Twelve inks were tested. The results of the tests are given in table 1. The inks containing ammonium ammoniumoxyferrigallate prepared according to the method of Silbermann and Ozorovitz [11] gave promising results. These inks are identified in table 1 as nos. 11 and 12, and the formulas are identical except that ink 12 is a weaker solution.

Tests of ink 12, made in duplicate, showed no significant harmful effect on paper. In addition to being the best ink tested as regards harmful effects on paper, this ink flowed well from a pen, did not form a sediment when exposed to the air for a month, and was only mildly corrosive to steel pens.

[6] R. H. Rasch, BS J.Research **3,** 476 (1929) RP107.
[7] R. H. Rasch, and G. O. Stone, Paper Trade J. **95,** T540 (July 1932).
[8] R. H. Rasch, and B. W. Scribner, BS J.Research **11,** 727 (1933) RP620.
[9] Tech. Assn. Pulp & Paper Ind., Paper Testing Methods, p. 62 (1929 ed.)
[10] Federal Specification TT-I-563; Ink, Writing.
[11] Bul. Soc. Stiinte **17,** 43–57 (1908); Chem. Zentrbl. **1908,** II, 1024.

The only other ink tested that was less harmful to paper than the standard ink was made with a sample of soluble prussian blue purified by dialysis. The dried material dispersed very readily in water and did not precipitate on standing for months. When this ink came in contact with iron, the prussian blue precipitated on the metal in large flocks, which makes the ink unfit for use with steel pens.

The data in table 2 show that the deleterious effects of ink on paper can be attributed to the iron salt and the mineral acid. There was no apparent correlation between the corrosion of steel and the effects on paper. It is also shown that the total corrosion of steel caused by an ink is not dependent exclusively on the amount of mineral acid in it, because the effect of gallic and tannic acids is too large to neglect. This observation agrees with F. F. Rupert's [12] findings. Data in table 1 indicate that inks made with hydrochloric acid are no more corrosive to steel than inks made with sulphuric acid.

The testing of the inks for sediment formation showed that the addition of gum arabic to ink apparently postponed the formation of sediment. Ink 2, containing no gum arabic, had after 2 weeks only a slight sediment, which increased slowly. On the other hand, ink 3, made according to the same formula except for the addition of 1 percent of gum arabic, showed no sediment until the end of the fourth week. However, after the sediment began to form, it accumulated very rapidly and formed a thick sludge.

The inks were tested for permanence on paper by exposing inked specimens to the carbon-arc light of a Fade-Ometer. All were found to be practically unimpaired as regards legibility during the life of the paper, which indicated good resistance to fading.

2. RELATIVE EFFECTS OF INKS ON DIFFERENT PAPERS

The deteriorative effects of inks 1, 2 and 3 on all of the papers were determined to find the relation between the composition of the paper and its susceptibility to deterioration by the action of the inks. A comparison of the deteriorative effect of inks 1, 2, and 3 on the seven different papers is shown in table 3.

TABLE 3.—*The effect of inks on the various papers*

Paper number	Fiber composition, percent				Sizing materials	Retention of folding endurance after heating, in percentage of initial			
	Rag	Sulphite		Highly purified wood fibers		Uninked	Inked		
		Bleached	Unbleached				Ink no. 1	Ink no. 2	Ink no. 3
1				100	Rosin and glue	83	51	41	62
2	60	40			Rosin	63	43	45	60
3	60	40			Rosin and glue	42	24	23	27
4		100			Rosin	42	0	16	17
5		50	50		do	23	8	9	8
6				100	Rosin and starch	98	48	55	74
7	100				Rosin and glue	72	50	54	52

The figures in the table do not show any consistent relationship between the quality of the papers and their resistance to the deteriorating action of ink. In general, the action of ink on the good record

[12] Ind.Eng.Chem. 15, 489 (1923).

papers, which, when uninked, were almost unaffected by the aging test, was much more serious than its action on a poor grade of paper, which deteriorated rapidly even when uninked. This tendency is shared with sulphur dioxide.[13] The kind of sizing had no significant effect on the resistance of the papers to the harmful action of the inks.

3. INFLUENCE OF INK ON ACIDITY OF PAPER

Some information on the increase in the acidity of the paper was obtained by testing inked and uninked specimens of paper no. 1, ruled with ink no. 1, before and after heating. The results of these tests are contained in table 4.

TABLE 4.—*Influence of ink on acidity of paper*

[Paper no. 1. Ink no. 1.]

Specimen	Acidity in terms of percent SO_3		Increase on heating	Total increase over original uninked specimen
	Before heating	After heating 72 hours at 100° C.		
	Percent	*Percent*	*Percent*	*Percent*
Uninked	.114	.123	8	8
Inked	.169	.220	36	93

While the data in table 4 were obtained on one paper and one ink only, they show that the total acidity of paper was increased by the use of a harmful ink; also, that the acidity of the inked paper increased much more rapidly under the accelerated-aging treatment than did that of the same paper uninked. High acidity accelerates the deterioration of paper fibers.

4. REPRODUCIBILITY OF RESULTS

Three different tests were made to determine the reproducibility of the results. These tests were made from 6 months to a year apart by different operators using different preparations of the same inks. The results of these tests, listed in table 5, are within the limits of the maximum deviation obtained in testing the untreated paper.

TABLE 5.—*Tests to show reproducibility of results*

[Paper no. 7]

Ink number	Date of test	Retention of folding endurance after heating 72 hr at 100° C.	
		Uninked paper	Inked paper
		Percent	*Percent*
2	Nov. 7, 1932	74	55
2, same lot	June 8, 1933	71	51
44	June 1, 1933	73	58
44, different lot	May 21, 1934	77	67
44-B	Aug. 25, 1933	61	61
44-B, different lot	May 21, 1934	74	66

[13] A. E. Kimberly, BS J.Research 8, 159 (1932) RP407.

V. SUMMARY AND CONCLUSIONS

Iron-gallotannate ink, prepared according to the government formula for standard writing ink, was found to greatly accelerate the deterioration of the papers in the heat test. The effect on papers suitable for permanent records, which deteriorated very little when uninked, was more apparent than on the papers of lower grade.

Of those inks tested, a type of ink containing ammonium ammoniumoxyferrigallate, prepared according to the method of Silbermann and Ozorovitz, had the least harmful effect on paper. This ink had good writing quality, was stable and only mildly corrosive to pens, and the deleterious effects on the paper were negligible. It appears to be a satisfactory record ink.

WASHINGTON, February 5, 1935

U. S. Department of Commerce · National Bureau of Standards

RESEARCH PAPER RP780

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

RECENT STUDIES OF THE IONOSPHERE [1]

By Samuel S. Kirby and Elbert B. Judson

ABSTRACT

Results of ionosphere measurements utilizing transmissions at vertical incidence and made weekly over a period of 18 months are discussed. Typical graphs of diurnal variations of the E-layer critical frequency and its relation to the ionizing force of the sun are shown for three seasons. Similar graphs for the F_2 layer are included as well as a seasonal curve of midday, and maximum critical frequencies of this layer. The absence of midday F_2 critical frequencies during the summer is pronounced.

A sporadic E layer appearing at the same virtual height as the normal E, and after the normal E has reached its critical penetration frequency, is discussed. A comparison of its appearance with local thunderstorms, is tabulated.

The presence of a tentatively named G layer is indicated.

CONTENTS

		Page
I.	Introduction	469
II.	E layer	471
III.	F_2 layer	475
IV.	Sporadic E	478
V.	G and higher layers	483
VI.	Conclusions	486

I. INTRODUCTION

Observations of the virtual heights of the ionosphere, made one day each week and extending over a period from June, 1933 to November 7, 1934 have presented an opportunity to continue the study of diurnal and seasonal effects and to compare them generally with other natural phenomena. Furthermore, other new and interesting phenomena have been observed, wholly due to the continuity of a day's "run" over a large range of frequencies. The purpose of this paper is to present and interpret this series of data.

The method employed in the experiment is essentially that of Breit and Tuve with modifications of technique similar to those described by Kirby, Berkner, and Stuart.[2]

Some data for diurnal variations of E critical frequencies have been contributed by T. R. Gilliland [3] of the National Bureau of Standards, from records of ionosphere heights made by his automatic recorder operating over a range of frequencies from 2,500 to 4,400 kc/s. Since these continuous records were available in this band of frequencies, no manual measurements between these limits were necessary.

[1] Presented in part at the Ninth Annual Convention, Institute of Radio Engineers, Philadelphia, Pa., May 27-30, 1934.

[2] Kirby, Berkner, and Stuart, BS J.Research **12**, 15 (1934) RP632; also Proc.Inst.Radio Engrs. **22**, 481 (1934).

[3] Gilliland, BS J.Research **11**, 561 (1933) RP608; also Proc.Inst.Radio Engrs. **22**, 236 (1934).

It has been well established that in the latitude of Washington there are two major layers in the ionosphere at all times and a third present in the daytime, especially during the summer. The first two are known as the E layer, 100 to 120 kilometers above the earth, and the F_2 layer, at approximately 230 to 350 kilometers virtual height. The third or F_1 layer appears at heights of 180 to 240 kilometers. Earlier experiments indicate that radio-frequency energy is returned to earth from these layers by a process of refraction, and these conclusions are further substantiated by the data herein given. The sharp rise in virtual height occurring at the critical penetration frequency and magneto-ionic double refraction which is observed in the F_1 and F_2 layers, indicate refraction. When magneto-ionic double refraction is observed, the critical frequency occurring at the lower frequency is the ordinary ray while the one at the higher frequency is the extraordinary ray. These phenomena are clearly shown in the graphs in figure 1. Although well-defined critical penetration frequencies are usually found in the E region, no evidence of magento-ionic double refraction has been observed.

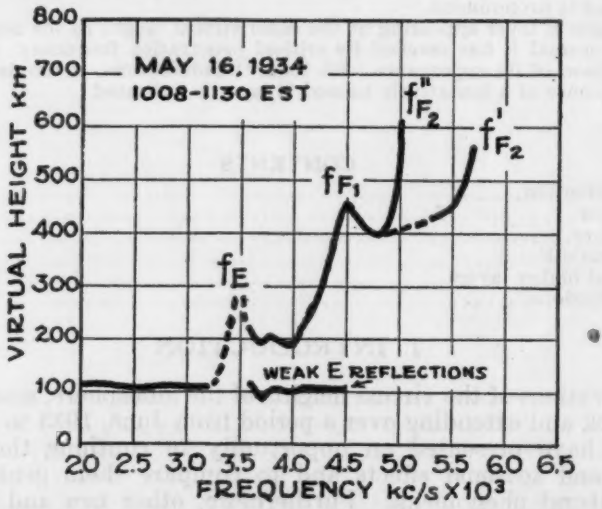


FIGURE 1.—*Typical frequency sweep and the three major layers,* E, F_1, *and* F_2, *with their critical frequencies.*

The critical or penetration frequencies are indications of the maximum ionization density of the layers and are defined as the lowest radio frequency of a wave which penetrates a layer at normal incidence.

The relation between the maximum electron density and critical frequency for the ordinary ray in any layer in the absence of dissipation is given by the well-known equation:

$$N=\frac{f''^2_c \pi m}{e^2}.10^6 \tag{1}$$

$$=1.24\, f''^2_c\, .10^{-2} \tag{1a}$$

where

N=number of ions per cubic centimeter.
f''_c=critical frequency of ordinary ray in kc/s,
m=mass of ion in grams,
e=charge on the ion in electrostatic units.

The relation between the critical frequencies for the ordinary and extraordinary rays is given by the well-known equation:

$$f_e''^2 = f_e' (f_e' - f_H) \tag{2}$$

where

f_e' = critical frequency for the extraordinary ray,

$$f_H = \frac{He}{2\pi mc} \times 10^{-3} \text{ kc/s} \tag{3}$$

$f_H \cong 1{,}460$ kc/s at Washington for electron ionization.

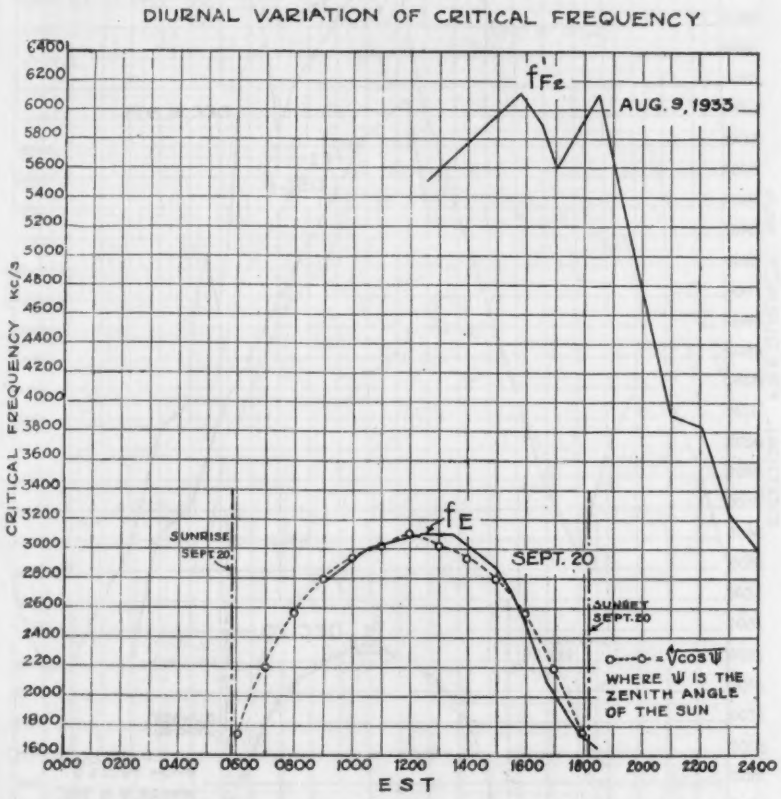


FIGURE 2.—*Typical curves of diurnal variation of critical frequencies of* E *and* F_2 *layers for fall.*

An indication of the diurnal variation of critical frequency for the various layers, corresponding to different seasons of the year, is given in the graphs of figures 2, 3, and 4.

II. E LAYER

E-layer critical-frequency measurements were made at frequencies of 2,500 kc/s or lower at early and late hours of day, and at night. Data for higher frequencies measured nearer noon were taken from Gilliland's records. The critical frequency of the normal E layer is most clearly in evidence during the fall, winter, and spring. During

the summer it is frequently obscured by the sporadic E, which will be discussed later. The lower graphs of figures 2, 3, and 4 are for the E layer.

The normal E critical frequency rises rapidly out of the broadcast band above 1,500 kc/s shortly after sunrise, comes to a broad maxi-

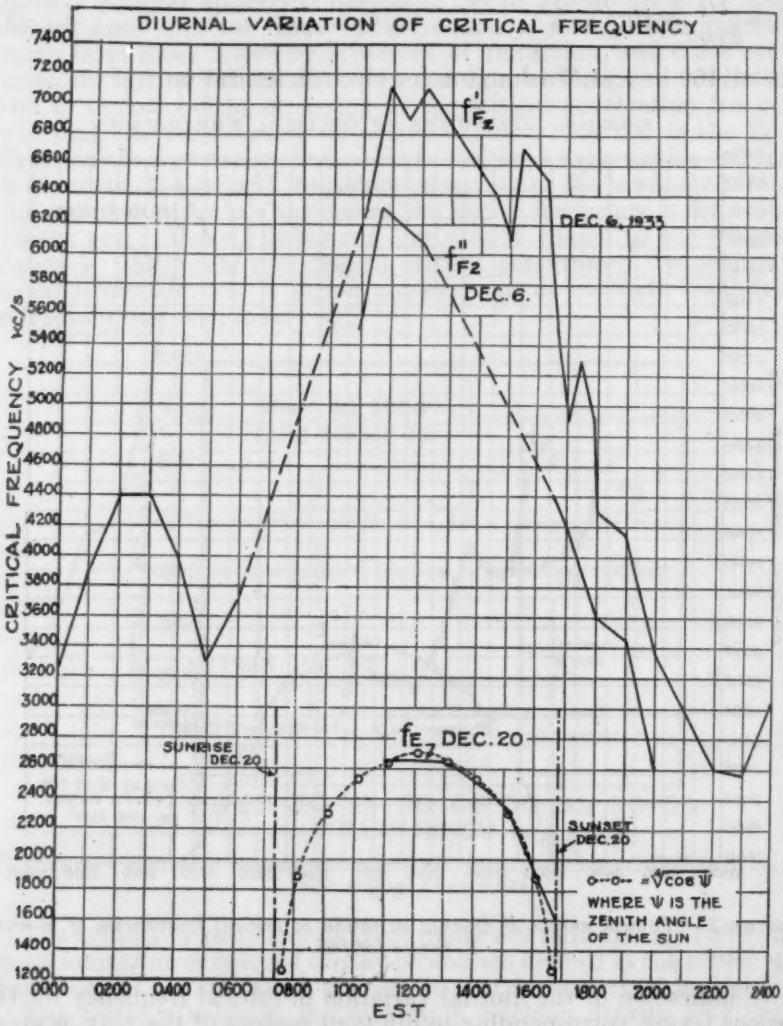


FIGURE 3.—*Typical curves of diurnal variation of critical frequencies of* E *and* F_2 *layers for winter.*

mum at noon, and falls rapidly into the broadcast band just before sunset. The graph of critical frequency versus time of day is approximately symmetrical about the noon axis. These facts indicate a rapid recombination of ions and that the ionization density is a simple function of the ionizing force of the radiation from the sun during most of the time between sunrise and sunset. If recombination is rapid it

may be shown from results of Pedersen [4] that the normal diurnal variation of f_c'' should follow the relation of $f_c''=f_c''$ max $(\cos\psi)^{\frac{1}{4}}$, where ψ is the angle which the sun's rays make with the zenith. Data taken during the period preceding and following the eclipse of August 31, 1932, were found to agree well with this relation.[5]

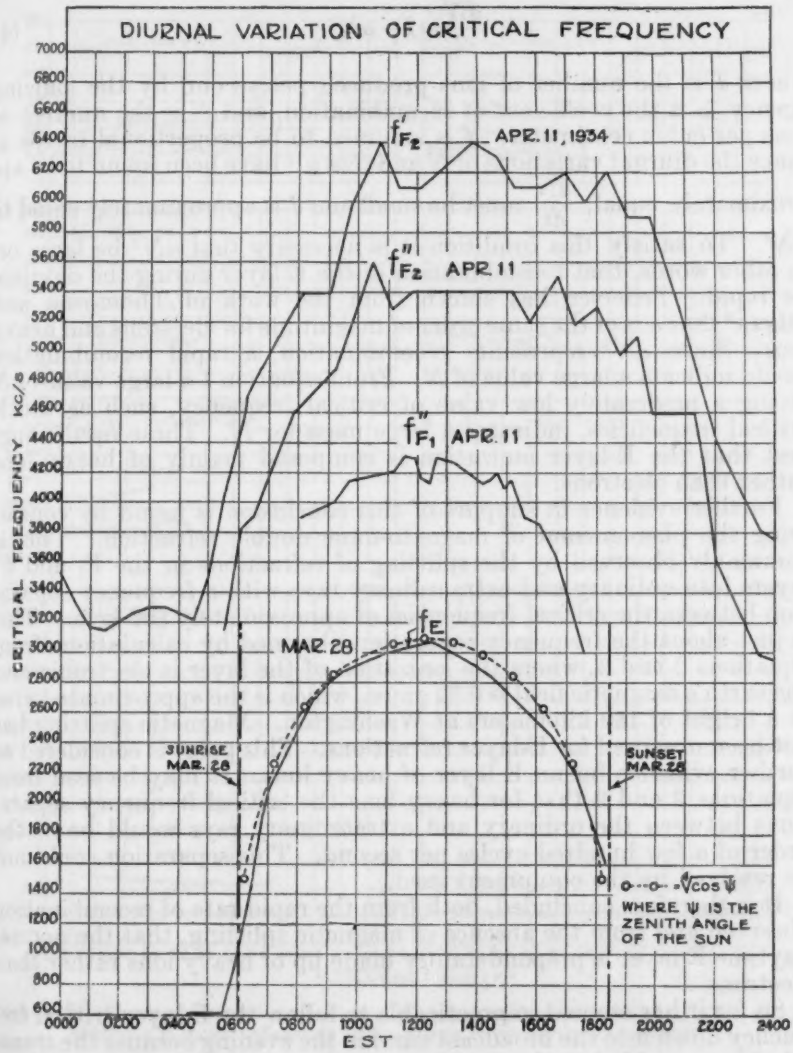


FIGURE 4.—*Typical curves of diurnal variation of critical frequencies of* E *and* F_2 *layers for spring.*

The lower graphs of figures 2, 3, and 4 show the diurnal variation of f_E (critical frequency for the E layer), determined experimentally and also the diurnal variation of $(\cos\psi)^{\frac{1}{4}}$ plotted in arbitrary units.

[4] Pedersen, Propagation of Radio Waves. Chapters V and VI.
[5] Kirby, Berkner, Gilliland, and Norton, BS J.Research **11**, 829 (1933) RP629; also Proc. Inst. Radio Engrs. **22**, 247 (1934).

From these figures it may be seen that the diurnal variations of f_x and $(\cos \psi)^{\frac{1}{2}}$ are approximately the same during most of the time that the sun is above the horizon. Also from equation 1 these figures indicate that N is proportional to $(\cos \psi)^{\frac{1}{2}}$ during most of the day.

The rate of change of ionization density may be expressed by

$$\frac{dN}{dt}=I-\alpha N^2 \tag{4}$$

where I is the number of ions produced per second by the ionizing agency, α is the coefficient of recombination, and N is the number of ions per cubic centimeter. I is assumed to be proportional to $\cos \psi$. Since the diurnal variations of N and $(\cos \psi)^{\frac{1}{2}}$ have been found to be approximately equal, $\frac{dN}{dt}$ must be small and I is approximately equal to αN^2. To satisfy this condition it is necessary that αN^2 be large or, in other words, that recombination in the E layer during the daytime be rapid. Pedersen has shown from the work of Thompson and others [6] that α is of the same order of magnitude for electrons and heavy ions. Since αN^2 represents recombination, a rapid recombination would indicate a large value of N. From equation 1 a large value of N giving a moderately low value of critical frequency, such as the E critical frequencies, indicates a large mass for N. These results suggest that the E-layer ionization is composed mainly of heavy ions rather than electrons.

Further evidence in support of this conclusion is found by considering the phenomenon of magneto-ionic double refraction. This is commonly observed by the splitting of refractions in the F_1 and F_2 layers into ordinary and extraordinary rays with a frequency separation between the critical frequencies of approximately 800 kc/s. This is just about the frequency separation obtained by calculations from equations 2 and 3, where the ionization of the layer is electronic and the earth's magnetic field is 0.52 gauss, which is the approximate value at a height of 180 kilometers at Washington. Magnetic splitting has not been observed for E-layer refractions. This point is considered as further evidence for an E layer of heavy ions. It may be seen from equations 2 and 3 that for heavy ions the critical frequency separations between the ordinary and extraordinary rays would be of the order of a few hundred cycles per second. This separation could not be resolved by the equipment used.

It is therefore concluded, both from the rapid rate of recombination observed and from the absence of magnetic splitting, that the normal daytime E layer is preponderantly made up of heavy ions rather than electrons.

So far it has seemed impracticable to follow the E-layer critical frequency down into the broadcast band in the evening because the transmissions would interfere with reception of broadcast programs. Measurements in the band (600 to 1,500 kc/s) made between 2000 EST and sunrise show that the E layer is frequently penetrated at frequencies of 600 to 800 kc/s. No definite E critical frequency has so far been observed at night. This phenomenon will be discussed under the section on "sporadic E layer."

[6] Pedersen, Propagation of Radio Waves. Chapter V.

During the months May to August, E-layer critical frequencies below 2,500 kc/s during the early and late part of the day, if they existed, were usually obscured by sporadic E-layer reflections. Satisfactory measurements of diurnal variations were not obtained during these months at frequencies below 2,500 kc/s.

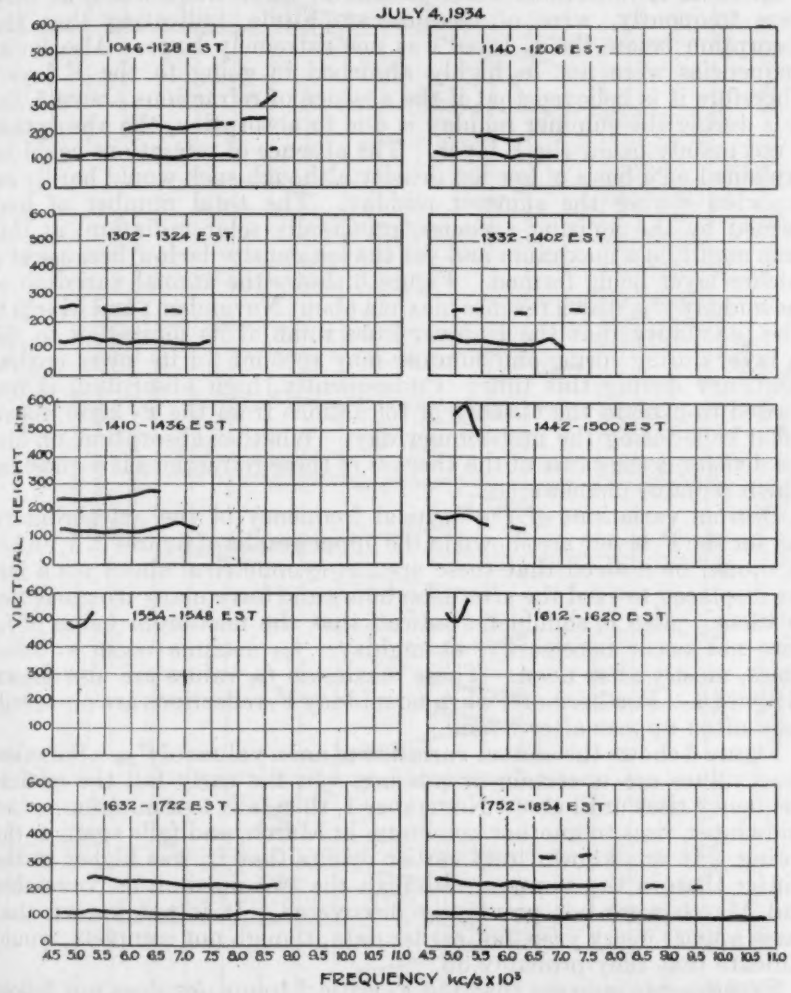


FIGURE 5.—*Curve showing the absence of F_2-layer refractions and the formation of sporadic E-layer reflections, often experienced during the summer.*

III. F_2 LAYER

Characteristics of the F_2 layer were discussed in an earlier paper.[7] Some additions to and modifications of the data and conclusions presented there are now desirable.

In general, midsummer, midday measurements of F_2-layer heights and critical frequencies were unsatisfactory. Frequently no reflec-

[7] Kirby, Berkner, and Stuart, BS J. Research **12**, 15 (1934) RP632; also Proc. Inst. Radio Engrs. **22**, 481 (1934).

tions or refractions could be received at frequencies above f''_{F1} (critical frequency of the ordinary ray for the F_1 layer) and sometimes none at lower frequencies. Figure 5 shows a typical summer-day run. The general absence of F_2 refractions at frequencies above 5,000 kc/s may be caused by absorption.

Sporadic E reflections when present at these frequencies, as they were frequently, were of medium amplitude, indicating that the absorption below the E layer was not extremely large. Also lower frequencies were not so highly absorbed in going to the E layer. Therefore it is believed that if the absence of refractions above 5,000 kc/s during the summer midday is due to absorption, the absorption is not mainly below the E layer. The absence of refractions could be explained on a basis of low ion density although such would hardly be expected during the summer midday. The total number of ions formed by the ionizing agencies, principally solar radiation, at this time might be a maximum and yet the ion density be low because of a thicker layer being formed. Figure 6 shows the annual variation of the midday f''_{F2} which reaches maxima about November 1 and March 1. The possibility that the F_2 layer loses some of its ionization to the F_1 layer during spring and summer may account for its lower critical frequency during this time. Consequently, high absorption is not needed to explain the absence of refractions from the F_2 layer above 5,000 kc/s during the midsummer day. Whether absorption or low ion density is the cause of the absence of these refractions is a question which remains unanswered.

Diurnal variations of f'_{F2} (critical frequency of the extraordinary ray for the F_2 layer) are shown in the upper graphs of figures 2, 3, and 4. It should be noticed that these are not symmetrical about noon but are displaced toward the afternoon hours and have many irregularities in them. Also it should be noticed that the maximum value of f_{F2} does not occur necessarily, at midday. f_{F2} maxima occur at other times, mostly after noon. These maximum f_{F2} values are also shown in figure 6. Furthermore, when no midday F_2 reflections are observed, they often appear after noon.

Figure 6 shows the annual variation of noon values of f'_{F2}. Summertime values are uncertain or missing. In the early fall the critical frequency rises until about November 1, then falls to a minimum after midwinter, rises to another maximum in March, and falls again in the spring. It was known from earlier results that f_{F2} was higher in the winter than in the summer, although the two maxima in November and March were not previously discovered. It is not known that these appear every year, but earlier data, though not complete, would indicate that they probably do.

Experiments indicate that the F_2 critical frequency does not follow closely in phase with the ionizing force of the sun, either diurnally or annually. That the sun has a major influence is shown by the diurnal variation from day to night, f'_{F2} rising rapidly after sunrise. The diurnal variations might be explained as a lag due to slow ionization and recombination, but the annual variations can hardly be explained on such a basis. From November to March the variations in the critical frequency of the F_2 layer are reasonably consistent with variations of the ionizing force of the sun.

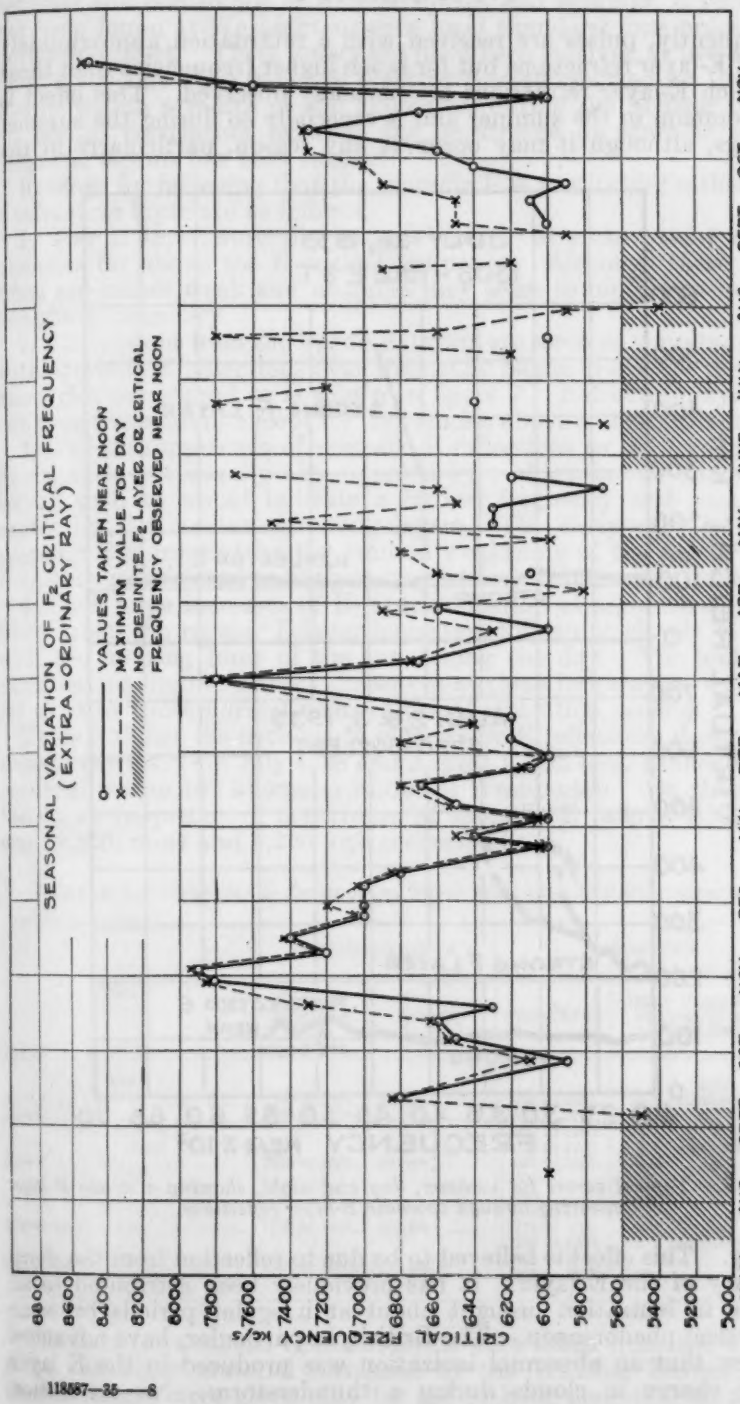


FIGURE 6.—*Seasonal variation of the critical frequency of the extraordinary ray for the F_2 layer at midday, and of the maximum critical frequency obtained for the day.*

IV. SPORADIC E

Frequently, pulses are received with a retardation approximately that of E-layer refractions but for much higher frequencies than those for which E-layer refractions are normally observed. This effect is very common in the summer and is especially so during the summer evenings, although it may occur at any season, particularly in the

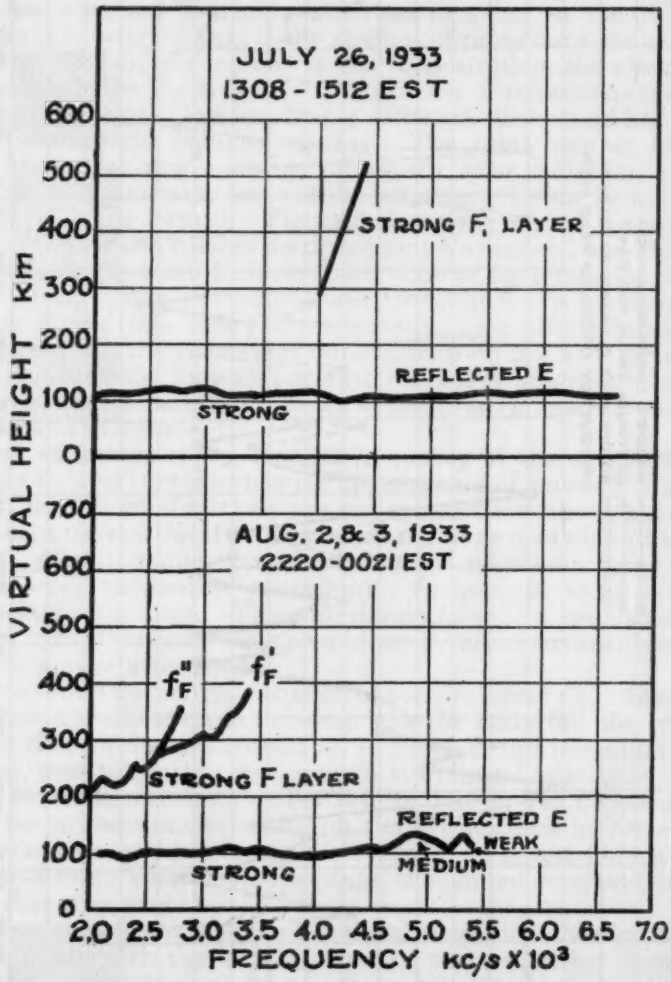


FIGURE 7.—*Typical curves for summer, day and night, showing a strong F layer appearing through sporadic E-layer reflections.*

evening. This effect is believed to be due to reflection from the sharp boundary of the E layer. It has previously been attributed to an increase in ionization brought about at irregular periods by some geophysical phenomenon. The British, in particular, have advanced the view that an abnormal ionization was produced in the E layer by the charge in clouds during a thunderstorm. No correlation

between the occurrence of thunderstorms and sporadic E reflection has been found at Washington; even local thunderstorms produce no noticeable effect. These reflections have been received at frequencies up to 9,400 kc/s when the U. S. Weather Bureau reported no thunderstorms within a radius of 300 kilometers during the 24-hour period. So far no correlation between the occurrence of sporadic E and magnetic storms has been found.

Reasons for believing that the sporadic E is a reflecting rather than a refracting layer are as follows:

1. The E layer normally returns energy to some extent at frequencies far above the E critical frequency. Although these reflections are rather weak and unstable they seem to indicate a more or less sharp boundary.

2. Refractions from the F_1 and F_2 layers are received simultaneously with sporadic E reflections over frequency bands of several thousand kilocycles per second as is shown in figure 7. Refracting layers are not thus transparent except for frequencies above a critical frequency.

3. The disappearance of sporadic E reflections as the frequency is increased is not usually accompanied by a sharp increase in virtual height such as would indicate a critical frequency and such as is shown by the regular refracting layers. The disappearance of the sporadic E is marked by the gradual weakening of the pulses as the frequency is increased until their amplitude falls below the noise level.

4. Such large increases of E-layer ionization at night do not seem likely when the regular E-layer ionization follows so closely in phase with the ionizing force of the sun during the day. The ionization densities required to refract the waves at these frequencies would be six to eight times normal noon values of ionization density.

Table 1 shows the occurrence of sporadic E reflections during local thunderstorms. On July 4, 28 and August 1, non-local thunderstorms occurred within 100 kilometer radius of Washington. On these days the upper frequency of occurrence of sporadic E (above 4,500 kc/s) was 10,800, none and 9,200 kc/s respectively.

TABLE 1.—*Sporadic E for days on which local thunderstorms occurred*

Date	Local thunderstorms		Sporadic E	
	Time of occurrence (EST)	Intensity	Time (EST)	Upper frequency of occurrence of sporadic E (above 4,500 kc/s)
1934				kc/s
April 4	1200 to 1500	Moderate	1040 to 2032	No E reflections.
June 6	1200 to 2200	do	1012 to 2148	Do.
June 27	1430 to 1530	Severe	0822 to 1230	8,400.
			1315 to 1430	No E reflections.
			1430 to 1524	No data; severe static.
			1526	4,500.
			1608	6,400.
August 15	1500 to 1600	do	1612 to 1709	8,800.
			1716 to 1740	7,000.
			1758 to 2206	No E reflections.
September 12	1200 to 1500	do	1003 to 1911	Do.
			1906 to 1927	5,000.

The data for nonlocal thunderstorms were taken from the weather maps and other material furnished by the Weather Bureau. The thunderstorms were given only for the 12-hour periods 0800 to 2000

and 2000 to 0800 EST and no indication of the intensity was given; some of the storms being indicated by a single clap of thunder. On July 4 the weather was locally fair, but one thunderstorm was reported just inside the 100-kilometer radius and another in the 100 to 200 kilometer zone. No precipitation was indicated so that it might be concluded that these were very minor storms. At about 1900 EST on the evening of July 4 sporadic E was found up to 10,800 kc/s, the highest so far recorded. This is shown in figure 5. Therefore close correlations in time between the occurrence of distant thunderstorms and sporadic E were not always possible. In the case of local thunderstorms, however, the time of occurrence was observed by us, and a fair estimate of the electrical intensity of the storm was also obtained. Therefore, if there is a correlation between the occurrence of thunderstorms and sporadic E, this correlation should be more positive for the case of local thunderstorms than for the thunderstorm data taken from the weather maps.

Table 2 shows the occurrence of sporadic E during the days on which no thunderstorms occurred within a radius of 300 kilometers of Washington. The above data fail to indicate a direct correlation between thunderstorms and sporadic E. Sporadic E is just about as prevalent on days when there are no thunderstorms within 300 kilometers as when there are severe local thunderstorms. Both phenomena are at a maximum during the summer months and this fact in itself suggests a correlation, but when the occurrences of thunderstorms and sporadic E are compared in more detail the correlation fails.

TABLE 2.—*Sporadic E for days on which no thunderstorms occurred within 300-kilometer radius during summer of 1934*

Date	Upper frequency of occurrence of sporadic E (above 4500 kc/s)
1934	kc/s
April 18	No E reflections.
May 2	Do.
May 9	Do.
May 16	Do.
June 13	7,000.
June 20	7,800.
July 11	8,000.
July 18	6,800.
August 8	9,200.
August 22	No E reflections.
August 29	7,500.

Another phenomenon believed to be a manifestation of the sporadic E layer occurred frequently during the early evening of the fall and sometimes winter on the frequency band 1,600 to 2,500 kc/s. This is illustrated by figures 8 and 9 for October 6, 1933 and January 3, 1934. The E-layer critical frequency was observed to drop below 1,600 kc/s (fig. 8, a, b, c) before sunset. E-layer reflections accompanied by strong F-layer refractions sometimes remained at frequencies above f_E as shown in figure 8. Later in the evening the E reflections became stronger and still later they weakened as in Figure 8 (f) and later disappeared. There usually was little question but that the second reflection was from the F layer rather than an E multiple. The second reflection was frequently stronger than the

first E, thus indicating that it was not a multiple of the first. The most prominent higher multiples were properly spaced to be multiples of the second reflection rather than the first. Also the F criticals sometimes appeared even while the E reflections were still present, figure 8 (e, f), but no critical was found for the lower reflections.

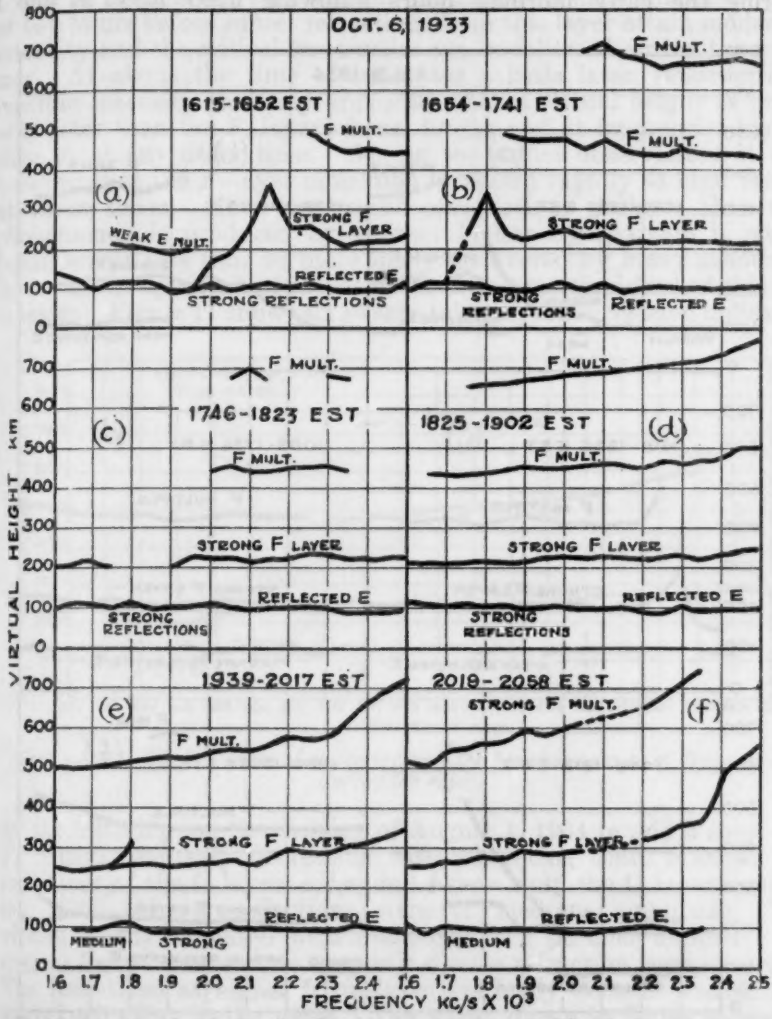


FIGURE 8.—*Typical fall curve showing simultaneous appearance of* F *refractions and sporadic* E*-layer reflections after the normal* E*-layer critical had passed.*

More frequently as f_E decreased during the early evening the E reflections became very weak or disappeared as shown in figure 8 (a, b, c). Later in the evening these E reflections became strong, figure 8 (c, d) while strong F layer refractions with multiples continued to come in, figure 8 (d, e). Usually except during the summer

the sporadic E disappeared from this frequency band later in the evening by a gradually weakening process and without showing a pronounced rise in virtual height such as indicates a critical frequency as shown in figure 8 (f).

Somewhat similar results have been observed in the broadcast band during the early morning hours following 0200 EST. E and F

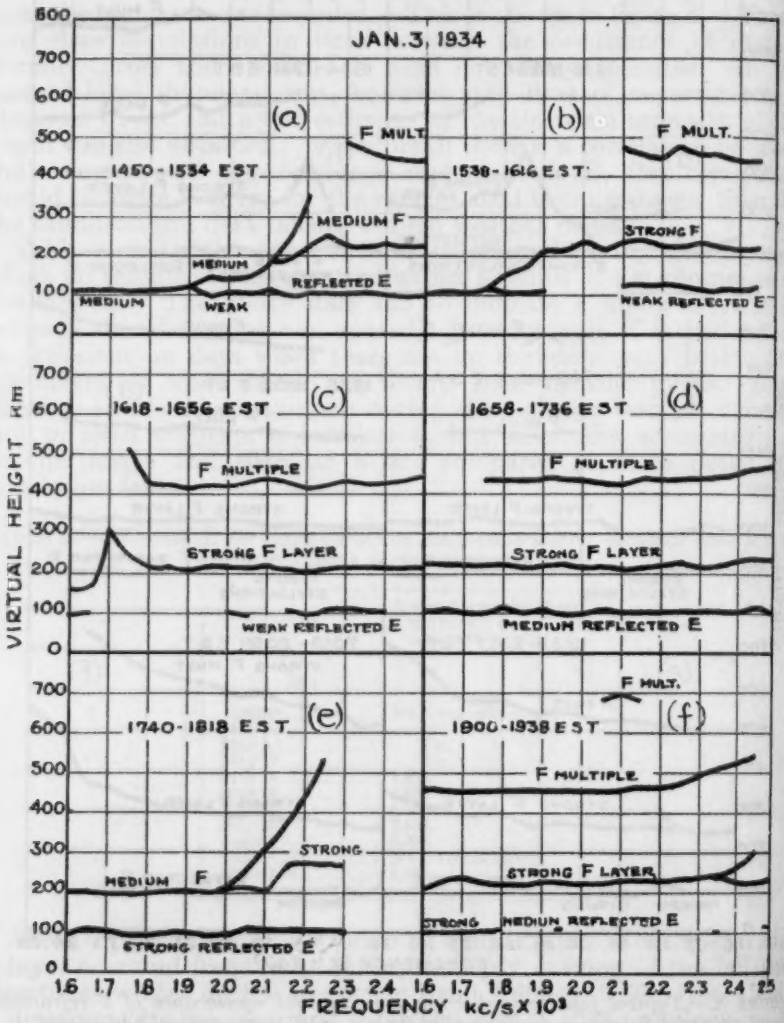


FIGURE 9.—*Typical winter curve showing simultaneous appearance of* F *refractions and sporadic* E*-layer reflections after the normal* E*-layer critical had passed.*

layers are frequently received simultaneously, no E critical frequencies were found and the disappearance of the E-layer reflections was marked by a gradual weakening rather than a critical and a sharp cut off. It is believed that during much of the time at night E reflections at broadcast frequencies are manifestations of the sporadic E

and the E critical f_s if it exists is frequently at a frequency lower than 600 kc/s. Figure 10 shows a typical night run of this kind.

V. G AND HIGHER LAYERS

The F_2 layer is not very evident during the summer midday. One or two hours before sunset refractions from this layer attain moderate intensity and the critical frequencies can be followed during the summer. At about the time of sunset or a little later, reflections of medium intensity suddenly appeared from a virtual height as great or greater than the F_2-layer virtual height and at frequencies higher than F_2 at any other time. During the earlier observations it was believed that the F_2-layer ionization increased rapidly to high values at these times. However, recent observations indicate that this phenomenon is produced by another higher layer, which is either found about this time or more likely uncovered by lower absorbing layers at the approach of sunset. We have tentatively called this the G layer. Figure 11 shows six sweeps taken in the succession indicated

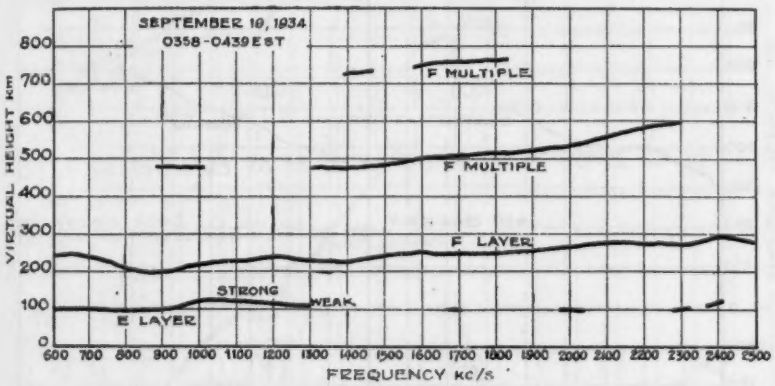


FIGURE 10. *Typical curve of sweep through the broadcast range of frequencies during the night.*

by the lettering, on the evening of August 1, 1934; a and b show the F_2 critical frequency decreasing with advancing time; b shows the formation of the G layer; c,d,e, and f show only the G layer remaining. The G-layer reflections were of medium amplitude. The virtual height increased with frequency in a peculiar manner. No critical frequencies and no magnetic double refraction were observed. The reflections at higher frequencies gradually became weaker and were finally lost in the noise. The effect shown in figure 11 occurs on summer evenings.

An additional effect which has been found at other seasons during both day and night [8] is shown in figure 12 for November 10, 1933. Complex reflections are returned from great virtual heights at frequencies above the F_2 critical frequencies. The virtual height versus frequency graphs have the characteristic slope found for the G layer during the summer evening and these reflections were probably from the same layer. The reflections shown in figure 12 were

[8] Kirby, Berkner, and Stuart, BS J.Research **12**, 15 (1934) RP632; also Proc.Inst.Radio Engrs. **22**, 481 (1934).

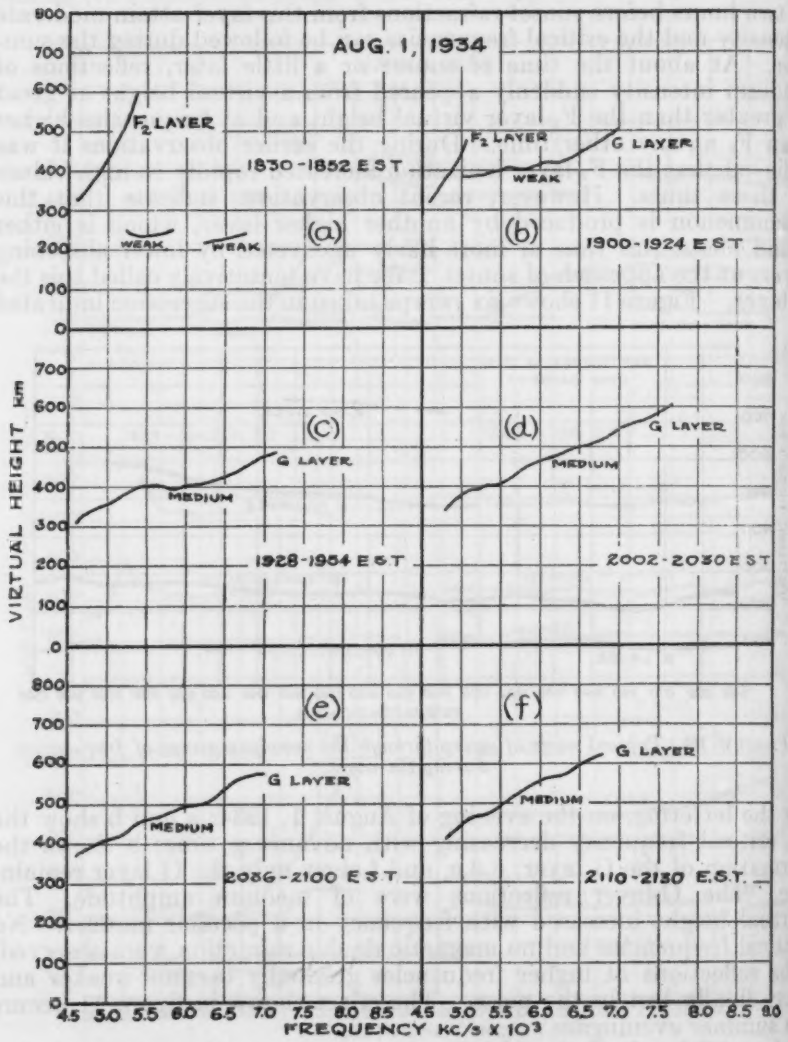


FIGURE 11. *Formation of the* G *layer during a summer evening.*

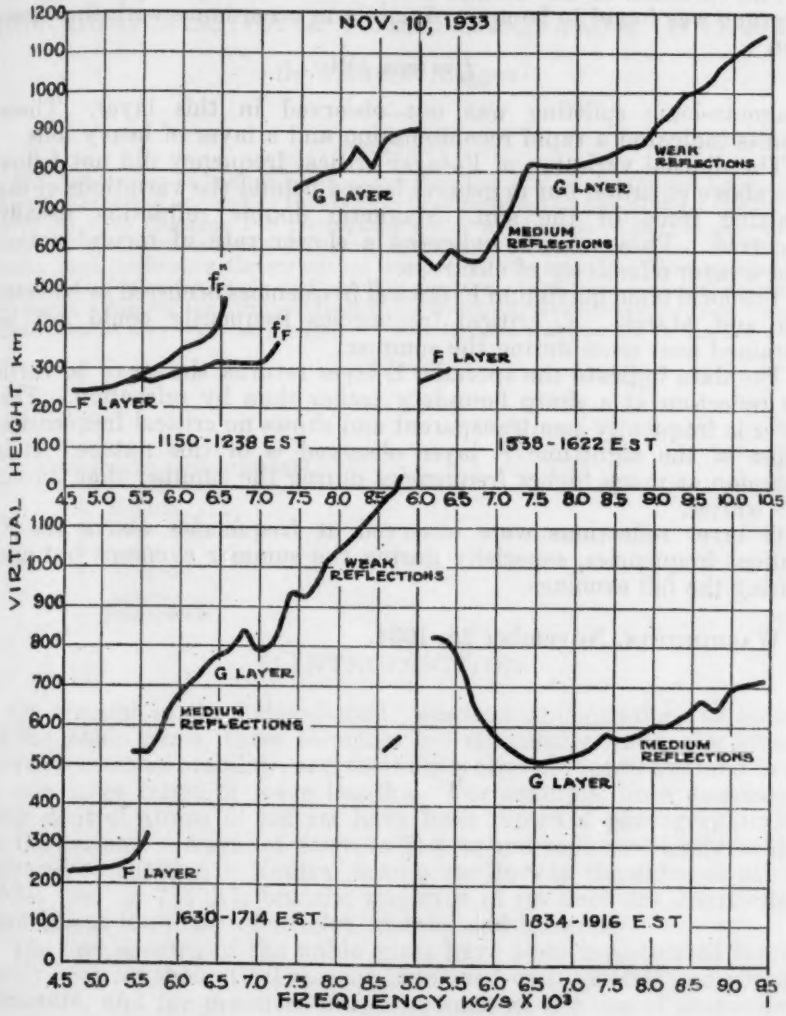


FIGURE 12. *G-layer reflections for a winter day.*

usually weaker than those of figure 11 and were complex, so that even if they were present during the summer they would be more likely to be lost in the higher noise background.

VI. CONCLUSIONS

The variation of the normal E-layer critical frequency during the daytime was found to be approximately in accordance with the equation

$$f_E \approx (\cos \psi)^{1/4}$$

Magneto-ionic splitting was not observed in this layer. These results indicated a rapid recombination and a layer of heavy ions.

The diurnal variation of F_2-layer critical frequency did not follow the above equation but in general lagged behind the variations of the ionizing force of the sun. Magnetic double refraction usually occurred. These results indicated a slower rate of recombination and a layer effectively of electrons.

The local noon maximum F_2 critical frequencies occurred in November and March. F_2 critical frequencies frequently could not be obtained near noon during the summer.

The data indicate the sporadic E layer returns the wave to earth by reflection at a sharp boundary rather than by refraction. This layer is frequently semitransparent and shows no critical frequencies. Most of the nighttime E layer observed is of this nature. It is common at much higher frequencies during the summer than during the winter.

G layer reflections were observed at frequencies above the F_2 critical frequencies, especially during the summer evenings but also during the fall evenings.

WASHINGTON, November 26, 1934.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP781

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

INFRARED SPECTRA OF NOBLE GASES (10500 TO 13000 A)

By William F. Meggers

ABSTRACT

The first spectra of helium, neon, argon, krypton, and xenon, excited by uncondensed discharges in Geissler tubes, have been explored in the infrared (10500 to 13000 A) with Eastman I–Z photographic plates. In each spectrum new lines have been recorded, most of which are accounted for as combinations of established terms, thus confirming the structural analyses of the spectra. Two missing $2s$ terms are revealed for xenon and possibly one new f-type term each for neon and for argon. Among the stronger lines those which involve accurately determined relative terms may serve as preliminary standards of wave length in the infrared.

CONTENTS

	Page
I. Introduction	487
II. Wave-length measurements	488
III. Results	488
1. Helium	489
2. Neon	490
3. Argon	492
4. Krypton	494
5. Xenon	495
6. Impurities	496

I. INTRODUCTION

On account of the "closed-shell" electron configurations in atoms of the noble gases, these elements are chemically inert, the atoms have exceptional stability, and their characteristic spectra extend over a very large range of wave lengths. For example, lines associated with neutral atoms of helium have been recorded photographically in the extreme ultraviolet down to 515 A, and radiometrically in the infrared to 20582 A. Neutral neon gives lines in the extreme ultraviolet (587 to 744 A), but the majority of its lines are distributed throughout the near ultraviolet, visible, and infrared.

The first spectra of the noble gases have been investigated intensively both for theoretical reasons connected with spectral and atomic structure, and for practical purposes, such as the use of monochromatic radiations as wave-length standards in spectroscopy and as standards of length in metrology. Most of this work has been done photographically since this is the best method for studying the details of a spectrum, but it was greatly handicapped by the limited range of infrared sensitiveness of photographic materials. A great advance was made several years ago when the discovery of new photosensitizing dyes [1] displaced this practical limit from about 9000 to approxi-

[1] C. E. K. Mees, J.Opt.Soc.Am. 22, 204 (1932); 23, 229 (1933).

mately 11000 A. Now the recent success of the research laboratory of the Eastman Kodak Co., in the preparation of still better infrared sensitizers,[2] makes it practicable to photograph the spectra of ordinary laboratory sources to 13000 A.

The results obtained by employing Eastman I–Z plates for the photography of the first spectra of the noble gases are presented in this paper. Most of the new data represent combinations of spectral terms already established. They thus confirm the structural analyses, and lines involving accurately known relative terms may serve as temporary standards in the infrared.

II. WAVE-LENGTH MEASUREMENTS

Geissler tubes of the type supplied by Robert Goetze in Leipzig were used as light sources. They have been described in other publications,[3] and it is hardly necessary to repeat that by using them end-on an enormous intensity increase is obtained. The tubes were operated in the 40,000-volt secondary circuit of a transformer, the primary of which was connected to a 110-volt source and supplied with 4 to 5 amperes alternating current. Light from the end-on capillary was projected on the slit of a stigmatically mounted concave grating [4] having a radius of curvature of 21½ feet, 7,500 lines per inch, and a scale of 10.2 A per millimeter in the first-order infrared spectrum.

The infrared radiation was filtered into the spectrograph with a sheet of Jena RG 5 glass, 2 millimeters thick, after the first exposure showed that the selenium red glass used heretofore was not safe beyond 12200 A. No second-order spectra or Lyman ghosts were found on any of the following spectrograms, but Rowland ghosts accompanied some of the strongest infrared lines. An indication of the infrared sensitivity of I–Z plates is given by the fact that the helium line at 10830 A was flanked by Rowland ghosts to the 12th order, although the grating employed shows no trace of such ghosts with moderately overexposed lines.

Exposures to the Geissler tubes ranged from 20 to 24 hours. Wave lengths of lines thus recorded in the first-order spectrum were derived from measurements relative to iron-arc standards photographed in the third-order spectrum. An exposure of one second sufficed to impress the iron spectrum. The first-order spectrum lines were measured and calculated as if they belonged to the third order, and then these values were multiplied by 3 to convert them to their true values. The corrections for standard density of air were neglected since they were always less than 0.01 A, while the average probable error of the infrared wave-length measurement is several times larger.

III. RESULTS

Preliminary exposures of Eastman I–Z plates to metallic-arc spectra in which a continuous background from white-hot electrodes and oxides was visible, immediately gave the impression that the sensitizing resembled that of I–Q (xenocyanine) plates, except that the maximum was displaced toward longer waves. In both cases the

[2] C. E. K. Mees, J.Opt.Soc.Am. **25**, 80 (1935).
[3] W. F. Meggers and C. J. Humphreys, BS J.Research **10**, 428 (1933) RP540.
[4] W. F. Meggers and Kelvin Burns, BS Sci.Pap. **18**, 191 (1922) S441.

sensitizing band is very broad, in Q the maximum action is at 9700 A, while in Z it is near 10900 A. The Z plates were found inferior to Q for wave lengths below 10300 A, but they run well ahead at 10500 A, and appear to be more sensitive at 13000 A than the latter are at 12000 A. Since no new lines short of 10500 A were detected with I–Z plates, the results are given only for lines of greater wave length. The data are presented in the following tables, in which successive columns contain estimates of relative intensity, measured wave lengths, wave numbers in vacuum, term combinations, and numerical differences of the terms. The intensity estimates are not corrected for variations in the photographic spectral sensitivity and as usual are comparable only over more or less limited regions.

In each table, the vacuum wave number (column 3) is derived from the observed wave length (column 2) by converting the wave length in air to vacuum value by means of the atmospheric-dispersion formula of Meggers and Peters,[5] and then calculating its reciprocal.

The modern quantum notation for spectral terms is used for helium, while for the remaining noble gases the notation is that first employed by Paschen [6] for the representation of neon terms.

1. HELIUM

Previous knowledge of the first spectrum of helium has been summarized in treatises on spectral series,[7] and in a paper on the infrared spectra photographed with xenocyanine.[8] Observations for the longer waves are displayed in table 1. For the sake of completeness, some lines probably due to He_2 molecules are included, but no attempt has been made to classify them. Values for the $2\ ^3S–2\ ^3P$ group at 10830 A are quoted from another paper;[9] they represent interferometer comparisons with neon standards.

[5] W. F. Meggers and C. G. Peters, BS Sci.Pap. **14**, 722 (1918) S327.
[6] F. Paschen, Ann.Physik **60**, 405 (1919).
[7] A. Fowler, Series in Line Spectra, page 91 (Fleetway Press, London, 1922). F. Paschen and R. Goetze, Seriengesetze der Linienspektren, page 26 (Julius Springer, Berlin, 1922). W. Grotrian, Handbuch der Astrophysik, **3**, 555 (Julius Springer, Berlin, 1930). R. Bacher and S. Goudsmit, Atomic Energy States, page 220 (McGraw-Hill, New York, 1932).
[8] W. F. Meggers and G. H. Dieke, BS J.Research **9**, 121 (1932) RP462.
[9] W. F. Meggers and C. J. Humphreys, BS J.Research **13**, 293 (1934) RP710.

TABLE 1.—*Infrared spectra of helium*

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
1?	12790. 9	7815. 9	3^1D–5^1F°	7815. 1
2	12784. 65	7819. 74	3^3D–5^3F°	7819. 89
3	12527. 40	7980. 32	3^3S–4^3P°	7980. 28
20	11969. 07	8352. 59	3^3P°–5^3D	8352. 59
6	11225. 83	8905. 59	3^1P°–6^1S	8905. 39
2	11065. 69	9034. 47		
40	11044. 95	9051. 44	3^1P°–6^1D	9051. 23
2	11017. 14	9074. 29		
30	11012. 97	9077. 72	3^1S–5^1P°	9077. 78
5	10996. 55	9091. 27	3^3D–6^3P°	9091. 44
50	10916. 98	9157. 53	3^1D–6^1F°	9157. 53
100	10912. 92	9160. 94	3^3D–6^3F°	9160. 94
1	10902. 1	9170. 04	3^1D–6^1P°	9170. 04
2500	10830. 341	9230. 793	2^3S_1–$2^3P^\circ_2$	9230. 79
1500	10830. 250	9230. 871	2^3S_1–$2^3P^\circ_1$	9230. 87
500	10829. 081	9231. 867	2^3S_1–$2^3P^\circ_0$	9231. 86
2	10753. 36	9296. 88		
3	10675. 68	9364. 52		
30	10667. 60	9371. 61	3^3P°–6^3S	9371. 66
1–	10653. 7	9383. 8		
1	10651. 48	9385. 79		
2	10644. 62	9391. 85		
3	10633. 50	9401. 67		
3	10618. 24	9415. 18		
3	10599. 17	9432. 12		
3	10576. 38	9452. 45		
2	10550. 06	9476. 02		
1	10504. 48	9517. 14		
2	10470. 28	9548. 22		
2	10433. 19	9582. 17		
2	10393. 30	9618. 95		
2	10350. 90	9658. 35		

2. NEON

To Paschen's [10] description and analysis of the neon spectrum a considerable extension was made when mesocyanine and xenocyanine plates were employed [11] in 1932. Additional lines have been found with I–Z plates (table 2), but these represent for the most part, combinations of established terms. Possibly one new term (3068.9) of 6*f* type is revealed, but a few lines of very low intensity remain unclassified in this and in the preceding lists of neon lines.

[10] F. Paschen, Ann. Physik **60**, 405 (1919).
[11] W. F. Meggers and C. J. Humphreys, BS J. Research **10**, 430 (1933) RP540.

TABLE 2.—*Infrared spectrum of neon*

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
1	12689. 2	7878. 56	$2p_3$–$2s_4$	7878. 54
2	12459. 49	8023. 81	$2p_5$–$2s_4$	8023. 87
15	12066. 38	8285. 22	$2p_6$–$2s_5$	8285. 28
10	11984. 99	8341. 49	$2p_2$–$2s_3$	8341. 53
10	11789. 93	8479. 50	$2p_7$–$2s_5$	8479. 54
50	11789. 11	8480. 09	$2p_6$–$2s_4$	8480. 12
60	11766. 87	8496. 12	$2p_2$–$2s_2$	8496. 13
10	11688. 08	8553. 39	$2p_1$–$3d_5$	8553. 485
80	11614. 18	8607. 82	$2p_5$–$2s_3$	8607. 87
25	11601. 62	8617. 13	$2p_3$–$2s_2$	8617. 14
50	11536. 41	8665. 84	$2p_1$–$3d_2$	8665. 865
90	11525. 11	8674. 34	$2p_7$–$2s_4$	8674. 38
150	11522. 82	8676. 06	$2p_4$–$2s_2$	8676. 07
1	11477. 33	8710. 44		
100	11409. 24	8762. 43	$2p_5$–$2s_2$	8762. 47
110	11390. 53	8776. 83	$2p_5$–$2s_5$	8776. 92
3	11366. 80	8795. 14	$2s_4$–$4p_8$	8795. 32
3	11333. 60	8820. 91	$2s_2$–$4p_5$	8820. 97
1	11329. 56	8824. 05	$2s_2$–$4p_2$	8824. 12
2	11304. 47	8843. 64	$2s_4$–$4p_7$	8843. 66
5	11303. 96	8844. 04	$2s_2$–$4p_4$	8844. 22
1	11298. 45	8848. 35	$2s_5$–$4p_{10}$	8848. 38
2	11293. 00	8852. 62	$2s_4$–$4p_6$	8852. 76
1	11261. 60	8877. 31		
300	11177. 59	8944. 02	$2p_9$–$2s_5$	8944. 10
10	11160. 29	8957. 89	$2s_5$–$4p_9$	8958. 02
300	11143. 09	8971. 72	$2p_8$–$2s_4$	8971. 76
4	11138. 55	8975. 37	$2s_3$–$4p_5$	8975. 57
4	11134. 62	8978. 55	$2s_3$–$4p_2$	8978. 72
5	11120. 37	8990. 05	$2s_2$–$4p_3$	8990. 16
2	11060. 88	9038. 40	$2s_5$–$4p_7$	9038. 50
20	11049. 80	9047. 46	$2s_5$–$4p_6$	9047. 60
15	11044. 06	9052. 17	$2s_2$–$4p_1$	9052. 43
10	11020. 93	9071. 17	$2s_4$–$4p_3$	9071. 32
1	10959. 6	9121. 9		
1	10937. 7	9140. 2		
1	10921. 16	9154. 03		
2	10891. 23	9179. 19		
8	10888. 53	9181. 46	$3d_1'$–6Z	9181. 6
5	10886. 35	9183. 30	$3d_1''$–6Z	9183. 4
200	10844. 54	9218. 71	$2p_6$–$2s_2$	9218. 72
3	10838. 30	9224. 01	$3d_2$–3068. 9	9224. 0
5	10819. 95	9239. 66	$3s_1''$–6U	9239. 92
4	10814. 83	9244. 03	$3d_2$–6Y	9244. 2
7	10808. 22	9249. 68	$3s_1'''$–6U	9249. 68
5	10806. 43	9251. 22	$3s_1''''$–6U	9251. 24
150	10798. 12	9258. 34	$2p_7$–$2s_3$	9258. 38
2	10789. 37	9268. 38	$3d_4$–3068. 9	9268. 4
6	10780. 57	9273. 41	$3d_3$–7Y	9273. 6
10	10766. 15	9285. 83	$3d_1'$–6W	9285. 93

TABLE 2.—*Infrared spectrum of neon*—Continued

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
12	10764. 09	9287. 60	$3d_1''$–6W	9287. 70
1	10760. 34	9290. 85	$3d_4$–6Z	9290. 9
2	10758. 28	9292. 63	$3d_4'$–6Z	9292. 7
1	10728. 8	9318. 15		
6	10690. 48	9351. 55	$3d_5$–6X	9351. 64
2	10673. 80	9366. 18	$3d_6$–6X	9366. 28
1	10664. 4	9374. 4		
40	10620. 70	9413. 00	$2p_7$–$2s_2$	9412. 98
200	10562. 43	9464. 93	$2p_1$–$3s_1'$	9464. 941

3. ARGON

Former knowledge of the first spectrum of argon is contained in papers published by Meissner [12] and in the infrared data presented [13] in 1933. A considerable extension of the latter is now given in table 3. Most of the new lines are accounted for as combinations of the known terms, and with the possible exception of 4W=5458.10, no new terms have been revealed. However, a few lines still await classification.

TABLE 3.—*Infrared spectrum of argon*

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
2	13008. 15	7685. 39	$2p_3$–$2s_2$	7685. 35
3	12956. 64	7715. 94	$2p_{10}$–$3d_5$	7716. 02
1	12933. 10	7729. 99	$2p_4$–$2s_3$	7729. 85
4	12802. 68	7808. 73	$2p_8$–$3d_1''$	7808. 71
2	12746. 13	7843. 38	$2p_4$–$2s_2$	7843. 34
3	12733. 39	7851. 22	$2p_8$–$2s_5$	7851. 08
7	12702. 26	7870. 46		
1	12621. 57	7920. 78	$2p_5$–$2s_2$	7920. 76
1	12553. 98	7963. 43	$2p_9$–$3d_1''$	7963. 28
15	12487. 67	8005. 71	$2p_9$–$2s_5$	8005. 65
15	12456. 13	8025. 98	$2p_8$–$2s_4$	8025. 82
20	12439. 34	8036. 81	$2p_{10}$–$3d_3$	8037. 00
2	12419. 36	8049. 74	$3d_3$–4X	8049. 51
20	12402. 83	8060. 47	$2p_7$–$3d_2$	8060. 36
4	12356. 24	8090. 86	$3d_3$–4Y	8090. 87
7	12343. 37	8099. 30	$2p_8$–$3d_1'$	8099. 49
3	12151. 30	8227. 32	$3d_1''$–4W	8227. 32
20	12139. 73	8235. 16		
25	12112. 31	8253. 81	$2p_9$–$3d_1'$	8254. 06
5	12026. 63	8312. 61	$2p_5$–$3s_1'$	8312. 67

[12] K. W. Meissner, Z. Physik **37**, 238 (1926); **39**, 172 (1926); **40**, 839 (1927).
[13] W. F. Meggers and C. J. Humphreys, BS J.Research **10**, 437 (1933) RP540.

TABLE 3.—*Infrared spectrum of argon*—Continued

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
25	11943. 50	8370. 46	$3d_5$–4X	8370. 49
3	11896. 60	8403. 47	$2p_6$–$3s_1''''$	8403. 58
5	11884. 47	8412. 04	$3d_5$–4Y	8411. 85
2	11879. 97	8415. 23		
20	11733. 26	8520. 45	$3d_6$–4X	8520. 59
30	11719. 51	8530. 44	$2p_8$–$3d_2$	8530. 29
3	11708. 22	8538. 67	$3d_2$–5X	8538. 74
5	11687. 61	8553. 73	$2p_7$–$3s_1''''$	8553. 87
4	11678. 47	8560. 43	$3d_2$–5Y	8560. 58
100	11668. 72	8567. 58	$2p_6$–$3s_1''$	8567. 56
8	11580. 39	8632. 92	$3d_4$–4W	8632. 91
150	11488. 12	8702. 27	$1s_2$–$2p_{10}$	8702. 20
30	11467. 57	8717. 86	$2p_7$–$3s_1''$	8717. 98
80	11441. 83	8737. 47	$2p_6$–$2s_2$	8737. 50
7	11398. 63	8770. 58	$3s_1'$–5Z	8770. 38
50	11393. 66	8774. 42	$2p_7$–$2s_3$	8774. 30
8	11248. 33	8887. 77	$2p_7$–$2s_2$	8887. 70
1	11209. 67	8918. 43	$3d_1'$–$4p_3$	8918. 46
2	11195. 37	8929. 82	$3d_3$–$4p_{10}$	8929. 92
2	11145. 40	8969. 86		
20	11133. 86	8979. 15	$3d_1'$–5V	8979. 13
20	11118. 75	8991. 36	$3d_1'$–5Y	8991. 55
60	11106. 44	9001. 32	$5d_1'$–5U	9001. 19
200	11078. 87	9023. 72	$2p_8$–$3s_1''''$	9023. 67
2	11075. 54	9026. 44		
1	11055. 40	9042. 88		
2	11043. 13	9052. 93	$3d_3$–$4p_8$	9052. 94
1	11028. 60	9064. 86	$2s_4$–5Y	9065. 06
1	10977. 30	9107. 22	$3d_2$–$5p_7$	9107. 41
2	10964. 00	9118. 26	$3d_3$–$4p_7$	9118. 23
120	10950. 74	9129. 30	$2p_6$–$3s_1'$	9129. 31
20	10947. 90	9131. 67	$3d_3$–$4p_6$	9131. 96
1	10911. 22	9162. 38		
1	10895. 9	9175. 3	$3d_4''$–$4p_4$	9175. 49
30	10892. 37	9178. 23	$2p_9$–$3s_1''''$	9178. 24
2	10885. 9	9183. 68	$3d_4''$–$4p_2$	9183. 68
150	10880. 96	9187. 88	$2p_8$–$3s_1''$	9187. 78
25	10861. 04	9204. 70	$2p_8$–$3s_1'''$	9204. 69
2	10845. 43	9217. 95	$2s_5$–5X	9217. 96
1	10837. 39	9224. 79	$3s_1'''$–6V	9224. 77
1	10831. 88	9229. 49	$3s_1'''$–6Y	9229. 59
1	10824. 00	9236. 20	$3s_1''$–6X $3s_1'''$–6U	9236. 04 9236. 42
1	10822. 74	9237. 28	$3d_2$–$5p_5$	9237. 54
6	10820. 18	9239. 46	$2s_5$–5Y	9239. 80
1	10812. 16	9246. 31	$3s_1''$–6Y	9246. 50

TABLE 3.—*Infrared spectrum of argon*—Continued

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
5	10807. 04	9250. 69	$3d_5$–$4p_{10}$	9250. 90
2	10795. 91	9260. 24	$3d_4''$–5X	9260. 40
1	10787. 4	9267. 5		
30	10773. 35	9279. 62	$2p_7$–$3s_1'$	9279. 60
15	10770. 35	9282. 21	$3d_4''$–5Y	9282. 17
60	10759. 13	9291. 88	$3d_4''$–5U	9291. 97
50	10733. 87	9313. 75	$3s_1'''$–5W	9313. 81
2	10732. 10	9315. 29	$3s_1'''$–5Z	9315. 22
6	10722. 22	9323. 87	$2p_{10}$–$3d_1''$	9324. 00
40	10712. 77	9332. 10	$3s_1''$–5Z	9332. 13
80	10700. 98	9342. 38	$2p_9$–$3s_1''$	9342. 35
50	10683. 40	9357. 76	$2p_8$–$2s_2$	9357. 72
200	10681. 78	9359. 18	$2p_9$–$3s_1'''$	9359. 36
500	10673. 55	9366. 43	$2p_{10}$–$2s_5$	9366. 37
1	10644. 9	9391. 6		
5	10634. 25	9401. 00	$3d_6$–$4p_{10}$	9401. 00
2	10623. 38	9410. 62	$3s_1''''$–6Y	9410. 61
1	10615. 7	9417. 43	$3s_1''''$–6U	9417. 44
2	10591. 23	9439. 13	$3d_5$–$4p_7$	9439. 21
1	10581. 63	9447. 75		
4	10576. 18	9452. 62	$3d_5$–$4p_6$	9452. 94
1	10559. 6	9467. 5		
50	10529. 32	9494. 69	$3s_1''''$–5W	9494. 83
2	10527. 34	9496. 48	$3s_1''''$–5Z	9496. 24
100	10506. 47	9515. 34	$3d_3$–4Z	9515. 46
200	10478. 10	8541. 10	$2p_{10}$–$2s_4$	9541. 11
500	10470. 051	9548. 43	$1s_3$–$2p_{10}$	9548. 36

4. KRYPTON

Complete information concerning the first spectrum of krypton[14] was summarized in 1933, when an extension to the infrared data was published.[15] Some additional lines (table 4) have been found on spectrograms made with I–Z plates, but most of them represent combinations of terms already known. In a few cases, the differences between observed and calculated wave numbers suggest a slight revision of term values. The term 2 s_5 (=13287.96), previously proposed on the basis of a single transition of the type $(p-s)$, is now confirmed by double-electron $(s-f)$ transitions, but two of the lines beyond 12000 still remain unclassified.

[14] W. F. Meggers, T. L. DeBruin, and C. J. Humphreys, BS J. Research **7**, 643 (1931) RP364.
[15] W. F. Meggers and C. J. Humphreys, BS J. Research **10**, 443 (1933) RP540.

TABLE 4.—*Infrared spectrum of krypton*

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
10	12204. 54	8191. 43		
3	12123. 56	8246. 15	$1s_2$–$2p_5$	8246. 153
4	12117. 81	8250. 06		
4	12077. 22	8277. 79	$3d_3$–4Z	8277. 62
10	11997. 15	8333. 03	$3d_3$–4Y	8333. 64
100	11819. 43	8458. 33	$2p_{10}$–$2s_5$	8458. 43
10	11792. 47	8477. 67	$2p_{10}$–$3d_2$	8477. 10
1	11655. 8	8577. 1	$2s_4$–5Z	8577. 00
1	11611. 6	8609. 7	$2s_4$–5Y	8609. 56
80	11457. 52	8725. 51	$2p_{10}$–$2s_4$	8725. 60
1	11333. 44	8821. 03	$2p_1$–$5d_5$	8821. 09
4	11328. 51	8824. 87	$3d_2$–5Z	8825. 43
1	11316. 1	8834. 6	$3d_2$–5X	8835. 06
1	11303. 8	8844. 2	$2s_5$–5Z	8844. 17
2	11262. 71	8876. 43	$2s_5$–5Y	8876. 73
50	11259. 16	8879. 23	$3d_5$–4X	8879. 48
80	11257. 74	8880. 35	$3d_5$–4Z	8880. 28
5	11214. 58	8914. 52	$3d_4$–$4p_8$	8914. 42
			$3d_4$–$4p_9$	8914. 70
40	11187. 13	8936. 40	$3d_5$–4Y	8936. 30
100	10874. 92	9192. 95	$3d_6$–4X	9193. 02
1	10801. 3	9255. 6		
2	10729. 43	9317. 61	$3d_3$–$4p_{10}$	9317. 63
20	10699. 33	9343. 82	$3d'_4$–$4p_9$	9343. 62
1	10647. 63	9391. 76	$3d'_1$–5Z	9391. 76
8	10626. 70	9407. 68	$3d'_1$–5U	9407. 80
20	10608. 43	9423. 89	$3d'_1$–5Y	9424. 32
100	10593. 01	9437. 60	$3d'_1$–5W	9437. 71
2	10575. 50	9453. 23	$3d_3$–$4p_8$	9453. 07
			$3d_3$–$4p_9$	9453. 35
1	10549. 64	9476. 40		
2	10486. 29	9533. 65	$3d_3$–$4p_7$	9533. 60
6	10458. 56	9558. 93	$3d_3$–$4p_6$	9558. 97

5. XENON

The most complete description and analysis of the first spectrum of xenon is that published by Humphreys and Meggers [16] in 1933. With xenocyanine (I–Q) plates, it was impossible to record lines beyond 11141 A, but with I–Z plates, 21 lines of greater wave length have been measured (table 5). Here also the majority of new lines is accounted for by known terms, but two new terms of $2s$ type are suggested. If the last observed line 12623.40 A is assumed to represent the transition $2p_{10}$–$2s_5$, the faint line at 11175.5 A is explained as the combination $2s_5$–$5p_8$, and the term $2s_5$ acquires a value of 12645.09. The line at 12235.24 A is similarly assumed to represent $2p_{10}$–$2s_4$, giving the term $2s_4$ a value of 12393.87, but unfortunately no lines remain with which to check it.

[16] C. J. Humphreys and W. F. Meggers, BS J.Research 10, 139 (1933) RP521.

TABLE 5.—*Infrared spectrum of xenon*

Intensity	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
5	12623. 40	7919. 63	$2p_{10}$–$2s_5$	7919. 66
1	12257. 81	8155. 83	$3d_6$–$3p_{10}$	8155. 85
5	12235. 24	8170. 88	$2p_{10}$–$2s_4$	8170. 88
3	12084. 80	8272. 60	$3d_4'$–$3p_8$	8272. 57
3	11953. 00	8363. 81	$3d_3$–$3p_6$	8363. 74
1	11951. 1	8365. 1	$3d_5$–$3p_9$	8365. 04
2	11912. 10	8392. 53	$3d_5$–$2p_4$	8392. 49
1	11874. 36	8419. 20	$3d_1'$–4Y	8419. 25
2	11857. 86	8430. 92	$2p_5$–$4d_5$	8430. 81
6	11857. 31	8431. 31	$3d_1'$–4Z	8431. 34
10	11793. 56	8476. 89	$3d_1'$–4U	8476. 89
50	11742. 26	8513. 92	$3d_1'$–4W	8513. 84
25	11614. 08	8607. 89	$3d_6$–$2p_4$	8607. 85
1	11537. 4	8665. 1	$3d_2$–$4p_5$	8665. 19
15	11491. 22	8699. 92	$3d_5$–$3p_6$	8699. 86
15	11415. 04	8757. 98	$3d_5$–$3p_7$	8757. 92
5	11309. 56	8839. 66	$3d_3$–$2p_3$	8839. 60
10	11289. 10	8855. 68	$3d_5$–$3p_5$	8855. 62
5	11214. 89	8914. 28	$3d_1''$–4X	8914. 18
1	11175. 5	8945. 7	$2s_5$–$5p_8$	8945. 73
10	11162. 67	8955. 98	$3d_3$–$2p_2$	8955. 95
50	11141. 09	8973. 33	$3d_6$–$3p_7$	8973. 28
8	11130. 81	8981. 62	$3d_1''$–4U	8981. 49
100	11127. 20	8984. 53	$3d_1''$–4V	8984. 46
250	11085. 25	9018. 53	$3d_1''$–4W	9018. 44
200	10895. 32	9175. 74	$3d_5$–$2p_3$	9175. 72
1000	10838. 34	9223. 98	$1s_4$–$2p_{10}$	9223. 986
100	10758. 86	9292. 13	$3d_5$–$2p_2$	9292. 07
150	10706. 78	9337. 32	$2p_6$–$4d_5$	9337. 31
20	10549. 76	9476. 30	$3d_2$–5Y	9476. 30

6. IMPURITIES

A small number of impurity lines were found on some of the spectrograms. Mercury and oxygen are fairly common contaminants of gases in Geissler tubes, and it happens occasionally that the glass becomes overheated to such a degree that sodium and potassium lines appear in the discharge. These impurity lines are listed in table 6. They are possibly of interest as additional or accidental standards in further infrared investigations of Geissler-tube spectra. In this table, the classification and calculated wave numbers are quoted from Atomic Energy States.[17] If the sodium and potassium lines observed here in low-pressure sources are compared with values reported for arcs at atmospheric pressure [18] they will be seen to be 0.41 A smaller, or 0.31 greater in wave number This difference may be regarded as a reasonable measure of the displacement due to one atmosphere of pressure.

[17] R. Bacher and S. Goudsmit, (McGraw-Hill, New York, 1932).
[18] W. F. Meggers, BS J.Research 10, 669 (1933) RP558.

TABLE 6.—*Infrared spectra of impurities*

Intensity and atom	λ_{air} A.	ν_{vac} cm^{-1} observed	Term combination	ν_{vac} cm^{-1} calculated
2 K	11772. 66	8491. 94	$4^2P^\circ_{1\frac{1}{2}}$–$3^2D_{2\frac{1}{2}}$	8495. 54
1 K	11689. 76	8552. 16	$4^2P^\circ_{\frac{1}{2}}$–$3^2D_{1\frac{1}{2}}$	8550. 51
5 Na	11403. 55	8766. 80	$3^2P^\circ_{1\frac{1}{2}}$–$4^2S_{\frac{1}{2}}$	8766. 15
3 Na	11381. 21	8784. 01	$3^2P^\circ_{\frac{1}{2}}$–$4^2S_{\frac{1}{2}}$	8783. 33
15 O	11302. 22	8845. 40	$^5P_3$–$^5S^\circ_2$	8847. 3
10 O	11297. 54	8849. 06	$^5P_2$–$^5S^\circ_2$	8850. 7
5 O	11294. 97	8851. 08	$^5P_1$–$^5S^\circ_2$	8853. 4
60c Hg	11286. 62	8857. 62	$^3S_1$–$^3P^\circ_0$	8857. 3

WASHINGTON, January 21, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP782

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

EFFECT OF CALCIUM CHLORIDE ON PORTLAND CEMENTS AND CONCRETES

By Paul Rapp[1]

ABSTRACT

To study the effect of the addition of calcium chloride on portland cements of widely varying composition, and on portland-cement concretes, a carefully controlled laboratory investigation was conducted. Such measurements as heats of hydration, setting times, consistencies and the strengths at various ages under several curing temperatures were made.

The addition of calcium chloride appears to increase somewhat the heat contributed at the end of 24 hours by dicalcium silicate and tetracalcium aluminoferrite and to decrease the heat contributed by tricalcium aluminate. Calcium chloride has but little effect on the heat contributed by tricalcium silicate. Calcium chloride increases the rate at which the heat is evolved from all cements. The strength contributed by the two silicate compounds in cement was increased and the strength contributed by tricalcium aluminate was decreased by the addition of calcium chloride. Calcium chloride decreased the time of set of 11 commercial cements and increased the flow and the strength of the resulting concrete. The physical properties of the experimental cements were similarly affected by the addition of calcium chloride. The optimum amounts to be added for different types of cement and at various curing temperatures are indicated.

CONTENTS

	Page
I. Introduction	499
II. Description of cements and calcium chloride	500
III. Effect of calcium chloride on the heat evolved during the first 24 hours of hydration	500
1. Heat of hydration of experimental cements	500
2. Heat of hydration of 11 commercial cements	502
IV. Effect of calcium chloride on the physical properties of mortars and concretes	504
1. Strength of experimental cements	504
2. Commercial cements	508
(a) Making the test specimens	508
(b) Test results	508
(1) Time of set	508
(2) Strengths	509
(3) Plasticity tests	512
V. Discussion and recommendations	513
VI. Summary	515
VII. References	517

I. INTRODUCTION

The Calcium Chloride Association, through its research fellowship at the National Bureau of Standards, has been investigating the effect of calcium chloride on portland cement and portland-cement

[1] Research associate at the National Bureau of Standards for the Calcium Chloride Association.

concrete. The investigation included a study of the influence of calcium chloride on the heat evolved up to 24 hours, and on the strength developed, by the major compounds present in portland cement. The comparative properties of mortars and concretes with different percentages of calcium chloride and at curing temperatures of 40, 70, and 90° F were also studied.

A progress report on these studies was presented at the thirteenth annual meeting of the Highway Research Board (1),[2] and a final report is given in this paper. A physico-chemical study of the reaction of calcium chloride with the alumina compounds of portland cement is being made, and will be reported separately.

II. DESCRIPTION OF CEMENTS AND CALCIUM CHLORIDE

Eight commercial portland cements (referred to in this paper as standard cements) together with one high-early-strength and two white portland cements were studied. In selecting these cements an effort was made to obtain the greatest practical variation in composition and physical properties.

Sixty experimental cements of varying composition and four commercial portland cements were furnished by the Portland Cement Association Fellowship at the National Bureau of Standards for certain heat and strength studies.[3] In the text of this report the cement compounds are abbreviated as follows:

Compound	Chemical formula	Abbreviation
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium alumino-ferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

Each of the cements furnished by the Portland Cement Association was ground to such a fineness that 12.5 percent was retained on the no. 200 sieve.

The calcium chloride used was a commercial product complying with the American Society for Testing Materials' Standard Specification D98–34. The amounts added to the cement are reported as percentages of anhydrous calcium chloride by weight of cement.

III. EFFECT OF CALCIUM CHLORIDE ON THE HEAT EVOLVED DURING THE FIRST 24 HOURS OF HYDRATION

1. HEAT OF HYDRATION OF EXPERIMENTAL CEMENTS

The samples of experimental cements had a wide range in composition, which made them of especial value in the present study. The analytical data and heats of hydration in the absence of calcium chloride were kindly furnished by the Portland Cement Association Fellowship. The quantity of each cement available was so limited that only one additional calorimetric determination (using one percent of anhydrous calcium chloride) could be made.

[2] Figures in parentheses here and elsewhere in the text refer to the references at the end of this paper.
[3] Table of the analyses of these cements as well as details of all the data will be published in the proceedings of the fourteenth annual meeting of the Highway Research Board.

The apparatus used for measuring directly the heat of hydration was that developed at the National Bureau of Standards (2).

The cement (200 grams) and water (67.5 grams) were thoroughly mixed in a small tinned can by a high-speed stirring device. Copper-constantan thermocouples were inserted into the mixture and the can was placed in a double-walled vacuum flask, which was in turn tightly closed and placed in an air thermostat maintained at 21° C. The temperatures were recorded by a multiple-junction recording potentiometer.

From the data obtained in this manner it was possible to calculate the heat evolved by the cement at any given period (3) in the 24 hour interval, having made the necessary correction for the radiation loss of the vacuum flask and its contents.

TABLE 1.—*Contribution of individual compounds to heat of hardening at 24 hours*

(Expressed as calories for each percent in 1 gram of cement)

Compound	Without $CaCl_2$	Probable error	With the addition of 1% $CaCl_2$[a]	Probable error
Tricalcium silicate	.80	±.02	.78	±.02
Dicalcium silicate	.19	±.02	.26	±.02
Tricalcium aluminate	1.62	±.07	1.47	±.06
Tetracalcium alumino-ferrite	.01	±.08	.25	±.06

[a] 1% anhydrous $CaCl_2$=1.3% commercial $CaCl_2$.

The contributions of the individual compounds to the heat of hardening were calculated, for the 60 experimental cements, by the method of least squares from the percentages of the compounds in the cements computed by the method of Bogue (4), assuming that a linear relationship exists between the compound composition of the cement and the heat evolved. The values obtained from these cements (table 1) show the same trends as those reported by Blank (5) and by Wood and coworkers (6), namely, that tricalcium aluminate evolves the greatest heat (expressed in calories for each percent present in each gram of cement), tricalcium silicate being next in order. The addition of calcium chloride increased somewhat the heat contributed by dicalcuim silicate and tetracalcium alumino-ferrite, had little or no effect on the heat contribution of tricalcium silicate, and decreased the heat contributed by tricalcium aluminate. The factors for the major cement compounds may be used to obtain a fairly accurate estimate of the increase in the rate of evolution of heat and the total heat evolved up to 24 hours for a particular cement when calcium chloride is added.

In order to illustrate the effect of change in compound composition upon the heat developed when calcium chloride is present table 2 was prepared. Column 1 of the table gives the grouping, column 2 the number of cements in each group, column 3 the average change in the heat developed in 24 hours produced by the addition of 1 percent of calcium chloride, and the remaining 4 columns the average compound composition. From this table it can be seen for the experimental cements that an increase in the heat evolved from group to group was accompanied by an increase in percentage of both the tricalcium aluminate and the tricalcium silicate, the two compounds shown from

table 1 to be those contributing the greater quantities of heat of hydration.

TABLE 2.—*Changes in the total heat evolved at 24 hours by the addition of 1 percent of calcium chloride to experimental cements*

Heat evolved in 24 hours without $CaCl_2$	Number of cements group	Average changes produced by 1% $CaCl_2$[a]	Average compound composition			
			Tricalcium aluminate	Tetracalcium alumino-ferrite	Dicalcium silicate	Tricalcium silicate
cal/g		cal/g	*Percent*	*Percent*	*Percent*	*Percent*
30 to 40	9	+7	3	15	47	30
40 to 50	12	+5	4	14	35	42
50 to 60	24	+4	10	12	34	42
60 to 70	16	0	10	11	25	52
70 to 80	3	−2	15	7	21	53

[a] 1% of anhydrous $CaCl_2$=1.3% of commercial $CaCl_2$.

Furthermore, the increase in the heat evolved because of the addition of 1 percent of calcium chloride is greatest in the first group (cements of lowest heat), becomes less in the succeeding groups, reaches zero in the fourth group, and in the fifth group there is actually a decrease of 2 calories per gram. These changes in heat evolved because of the addition of calcium chloride cannot apparently be assigned to the tricalcium silicate content in each group, since it has been shown in table 1 that each percent of tricalcium silicate present in 1 gram of cement evolves the same number of calories with or without calcium chloride. The changes do, however, appear to be inversely related to the amounts of tricalcium aluminate, and directly related to those of dicalcium silicate and tetracalcium alumino-ferrite present in each group, and in this respect are in agreement with the data of table 1.

2. HEAT OF HYDRATION OF 11 COMMERCIAL CEMENTS

The heats evolved during the first 24 hours of hydration were measured for 11 commercial cements without calcium chloride and also with the addition of 0.5, 1, 1.5, and 2 percent of anhydrous calcium chloride.

The heat data obtained from the 11 commercial cements, and from 4 samples of commercial cement supplied by the Portland Cement Association Fellowship, were analyzed in the same manner as the data obtained from the experimental cements. The results of the analysis showed that the heat contribution of the individual compounds, and the effect on the heat when calcium chloride was added, were much the same for these commercial cements as for the experimental cements.

The effect of the addition of calcium chloride on the heat developed by a typical portland cement (B) is shown in figure 1. As the amount of calcium chloride is increased, the initial rate of evolution of heat is increased, but the amount of heat developed at 24 hours does not differ by more than a few calories. The other 7 standard and the 2 white portland cements behave in a similar manner upon the addition of calcium chloride.

Time-heat curves plotted from the temperature data of these cements show that calcium chloride generally increases the initial

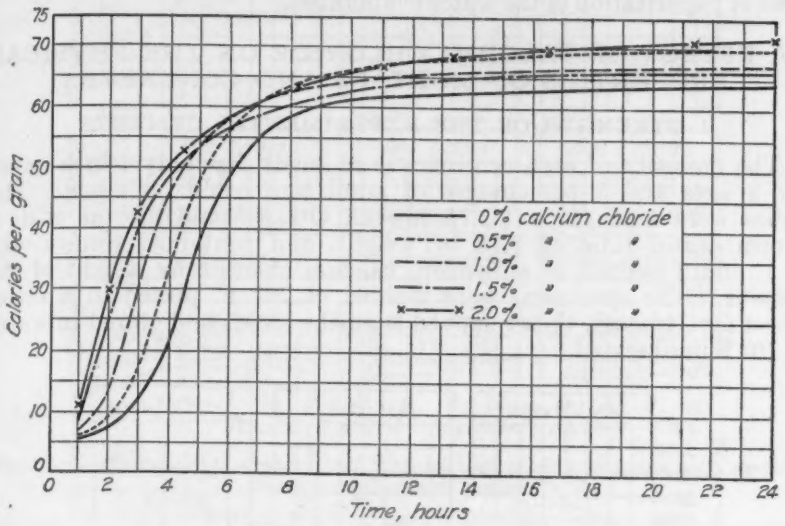


FIGURE 1.—*Typical heat curves.*

(Cement B).

rate of temperature rise and decreases the time required to reach the maximum temperature. However, with the high-early-strength

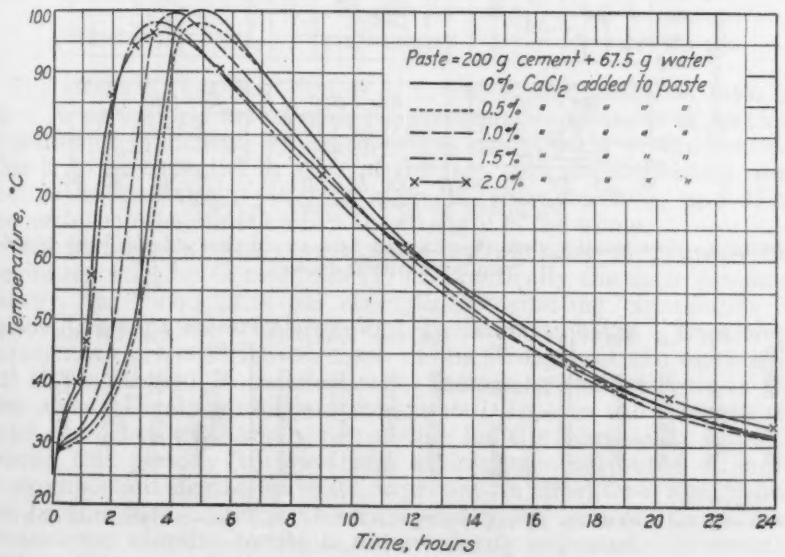


FIGURE 2.—*Temperature curves for high-early-strength cement.*

(Cement D)

cement (fig. 2), both with and without calcium chloride, the maximum temperature attained was at or near the boiling point of water.

Consequently the heat of hydration could not be ascertained satisfactorily since an undetermined portion of the heat was lost as the latent heat of vaporization of the water evaporated.

IV. EFFECT OF CALCIUM CHLORIDE ON THE PHYSICAL PROPERTIES OF MORTARS AND CONCRETES

1. STRENGTH OF THE EXPERIMENTAL CEMENTS

The quantity of each cement was so small that only 1-inch cubes for 3 ages and 3 percentages of admixture could be made. The cubes were made of a 1:2.75 pit-run Ottawa-sand mortar with a cement-water ratio of 1.73 by weight, and contained respectively 0, 1, and 2 percent of anhydrous calcium chloride by weight of the cement. The specimens were molded at 70° F, placed in a moist closet for 24 hours, then removed from the molds and stored in water at 70° F until tested.

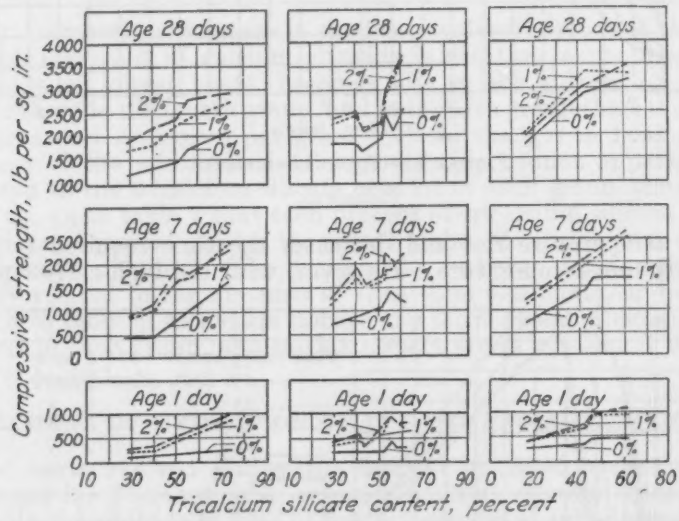


FIGURE 3.—*Compressive strength with and without calcium chloride with variable tricalcium silicate content.*

Cement no.	C_3S	C_2S	C_3A	C_4AF
45	28	52	0	15
6	41	39	0	14
11	51	29	0	15
46	56	24	0	16
61	56	24	0	16
62	74	5	0	15

C_3A=0%; C_4AF=14 to 16%

Cement no.	C_3S	C_2S	C_3A	C_4AF
41	29	49	7	12
24	41	37	7	12
4	43	34	7	13
59	52	26	6	13
9	53	25	7	13
60	55	20	7	12
60a	57	20	6	13
42	61	17	7	12

C_3A=6 to 7%; C_4AF=12 to 13%

Cement no.	C_3S	C_2S	C_3A	C_4AF
37	16	58	16	6
8a	42	33	15	7
57	45	28	15	7
38	61	14	14	7
58	62	13	14	7

C_3A=14 to 16%; C_4AF=6 to 7%

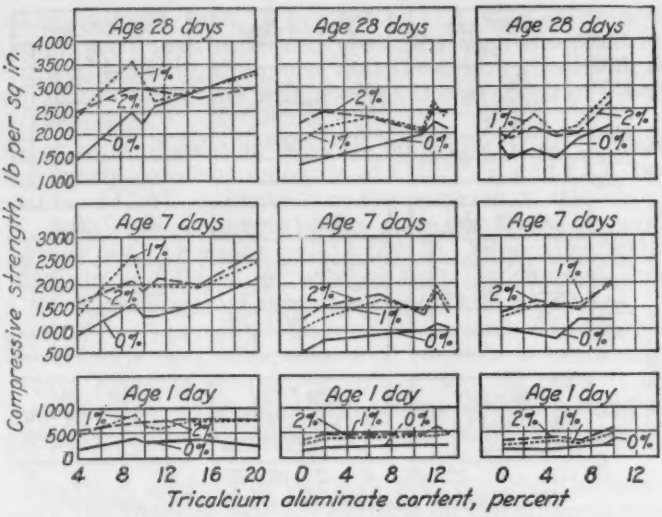


FIGURE 4.—*Compressive strength with and without calcium chloride with variable tricalcium-aluminate content.*

Cement no.	C_3S	C_2S	C_3A	C_4AF
50	47	37	4	8
16	42	38	9	6
53	47	35	10	4
28	44	34	11	6
57	45	28	15	7
8a	42	33	15	7
1a	45	28	20	4

C_4AF=4 to 8%

Cement no.	C_3S	C_2S	C_3A	C_4AF
6	41	39	0	14
51	38	45	2	13
4	43	34	7	13
24	41	37	7	12
29	40	33	11	13
12	41	32	12	12
20	42	30	12	13
30	39	32	13	13

C_4AF=12 to 14%

Cement no.	C_3S	C_2S	C_3A	C_4AF
19	44	33	0	19
27	41	35	1	20
17	39	37	3	18
23	38	33	5	20
13	38	31	7	21
21	40	30	10	17

C_4AF=17 to 21%

The strength results in figures 3, 4, and 5, and published tests by other investigators, reveal that the compressive strength of mortars is markedly influenced by the chemical composition of the cement. This is to be expected in view of the fact that the individual compounds have entirely different strength characteristics, and their proportions in the cement affect the strength of the whole.

The findings of this investigation corroborate, in general, the results reported by Gonnerman (7) on practically the same cements, namely, (a) "The principal strength contributing compounds of portland cement are tricalcium and dicalcium silicates. Tricalcium silicate not only contributed much of the strength at the early ages but also continued to be effective in increasing the strength at the later ages. Dicalcium silicate contributed little to the strength up to 28 days, but was largely responsible for the increase in strength beyond this period; (b) tricalcium aluminate contributed strength to an important degree up to 28 days, but its effect then diminished and became zero or negative at 1 and 2 years, and (c) the role of tetracalcium alumino-ferrite is not so clearly indicated. It contributed to some extent to the compressive strength of mortars and concrete at 28 days and later periods."

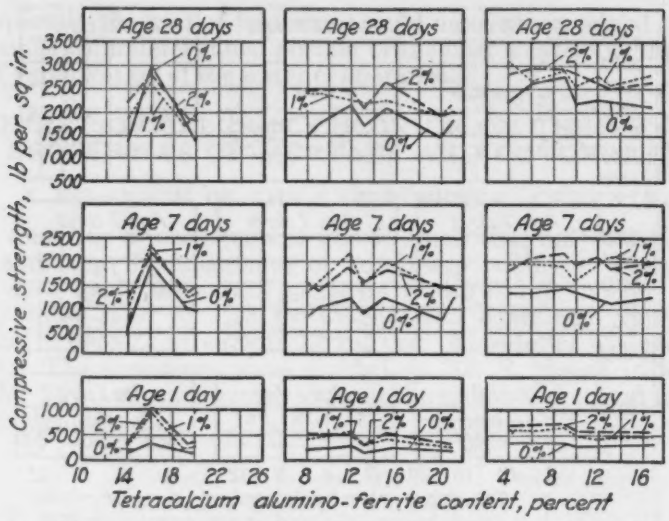


FIGURE 5.—*Compressive strength with and without calcium chloride with variable tetracalcium alumino-ferrite content.*

Cement no.	C_3S	C_2S	C_3A	C_4AF
6	41	39	0	14
58	39	40	2	16
19	44	33	0	19
27	41	35	1	20

C_3A=0 to 2%

Cement no.	C_3S	C_2S	C_3A	C_4AF
50	47	37	4	8
18	43	39	5	9
24	41	37	7	12
4	43	34	7	12
14	37	38	7	15
22	41	33	8	15
23	38	33	5	20
13	38	31	7	21

C_3A=4 to 8%

Cement no.	C_3S	C_2S	C_3A	C_4AF
53	47	35	10	4
28	44	34	11	6
34	41	36	11	9
35	41	33	11	9
3b	43	33	11	10
12	41	32	12	12
20	42	30	12	13
21	40	31	10	17

C_3A=10 to 12%

The relation between the silicate content of the cements and the compressive strength of the mortars, with and without calcium chloride, is shown in figure 3. The cements tested had a computed C_3S content ranging from 16 to 74 percent by weight and a C_2S content ranging from 5 to 58 percent. With the amounts of the other compounds maintained essentially constant, an increase or decrease in the C_3S content was accompanied by a decrease or increase in the C_2S content. The results (fig. 3) show that the addition of calcium chloride increased the mortar compressive strength at all ages of all the cements covering the exceedingly wide ranges in silicate content noted above.

The relation between the content of tricalcium aluminate and the compressive strength of the cement mortars, with and without calcium chloride, is given in figure 4. In order to study the effect of the C_3A content on strength, 3 groups of cements were selected in which the C_3A content varied, but the C_3S, C_2S, and C_4AF contents were held as constant as possible in each group. The C_4AF varied from group to group. A study of the data, (fig. 4), reveals that the action of calcium chloride on the C_3A does not affect the strength to any great extent until the C_3A content is increased beyond the amount encountered in commercial portland cements. Carlson and Bates (8) found the average amount of C_3A in 84 commercial cements to be 11 percent, ranging from 4 to 17 percent. Only 6 of the experimental cements had a C_3A content of 15 percent or more. Three of the

cements having more than 15 percent of C_3A with calcium chloride added (fig. 4) have greater 28-day strengths than the plain mortars. It is considered unlikely, therefore, that the action of calcium chloride on the tricalcium aluminate would affect the strength of present-day commercial cements.

Results of tests of calcium chloride on 3 groups of cements, each containing nearly constant amounts of C_3S, C_2S, and C_3A, but variable amounts of C_4AF, indicate that the presence of calcium chloride in the amounts studied increased the strength of the cements until the percentage of C_4AF was above 13 (fig. 5). Referring again to the data of Carlson and Bates (8) we find that the average amount of C_4AF in 84 commercial portland cements was 8 percent, ranging from 2 percent to 13 percent. Beyond 13 percent of C_4AF the action of calcium chloride on the experimental cements is not clearly indicated. Three cements containing 16, 19, and 20 percent of C_4AF have a lower strength at 28 days with calcium chloride, but 5 cements containing more than 13 percent of C_4AF have a greater strength with calcium chloride.

A mathematical analysis of the compressive-strength data reveals more clearly the effect of calcium chloride on the strength-contributing value of the individual compounds. The results of this analysis made by the method of least squares give factors (table 3) showing the contribution in pounds per square inch for each percent of the 4 major compounds. The analysis assumes a linear relationship between the percentage of each compound and the strength at a given age.

TABLE 3.—*Component compressive-strength factors, with and without calcium chloride, for sixty experimental cements*

$CaCl_2$	Age	Strength factors (pounds per square inch for each percent of component)				Difference between calculated and observed strengths,[1] expressed as probable error	
		C_3S	C_2S	C_3A	C_4AF		
Percent	*Days*					lb/in.²	*Percent*
0	1	4.09±0.36	0.22±0.38	10.4±1.1	−2.7±1.2	±37	16
1	1	13.03±0.79	−1.03±0.83	15.1±2.3	−10.9±2.7	±81	14
2	1	13.91±0.61	−1.06±0.65	16.2±1.8	−8.7±2.1	±63	10
0	7	20.8±1.2	−4.1±1.2	47.6±3.4	−0.2±3.9	±119	10
1	7	31.8±1.6	0.2±1.7	41.3±4.9	−1.2±5.5	±168	10
2	7	33.7±1.5	3.4±1.5	33.1±4.4	−7.0±5.0	±151	9
0	28	30.2±1.6	3.9±1.6	88.9±4.6	−3.6±5.3	±160	8
1	28	41.2±1.9	13.8±2.1	58.1±5.8	−12.6±6.6	±201	8
2	28	46.1±1.9	16.0±2.0	38.5±5.7	−18.8±6.5	±197	8

[1] For each cement the strength was calculated from the factors. The probable errors given are computed from the difference (d) between the calculated and observed strengths for each cement by the equation: Probable error $= .6745\sqrt{\frac{\Sigma d^2}{n-1}}$

Tricalcium silicate adds strength to the cements at all ages. Calcium chloride is effective in increasing the strength-contributing value of C_3S in cement at all ages tested. At 1 day the C_2S contributes little or nothing to the strength. At 7 days the effect is negative, but at 28 days there is a gain of approximately 4 lb/in.² for each percent. The addition of calcium chloride increases the strength-contributing factor of the C_2S at the ages studied although it shows little effect at 1 day. At 7 days 2 percent of anhydrous calcium

chloride increases the strength by about 7 lb/in.^{2} for each percent of C_2S, and at 28 days this strength is increased by about 12 lb/in.^{2}

Tricalcium aluminate adds to the strength at all ages up to 28 days. Calcium chloride increases the strength contributed by C_3A at 1 day, but it decreases the strength at 7 and 28 days. The decrease is larger with increasing amounts of calcium chloride and is largest at 28 days.

The strength contributed by C_4AF is so small and the probable error is such that it is not known whether the contribution is positive or negative at any age. The addition of calcium chloride apparently makes these factors negative.

Using the factors which give the strength contributed by the four major compounds in cement, and knowing the compound composition of the cement, a fairly accurate computation of the strength produced by the addition of calcium chloride can be obtained. Referring to table 3 we see that the strength can be calculated for all cases, with probable errors ranging from 8 to 16 percent. With 2 percent of anhydrous calcium chloride the precision of the computed strength varies from 8 to 10 percent.

2. COMMERCIAL CEMENTS

(a) MAKING THE TEST SPECIMENS

The standard evaluation tests for portland cement (9) were made, except that 2-inch mortar cubes were substituted for briquettes. In these tests 0, 0.5, 1, 1.5, and 2 percent of anhydrous calcium chloride, respectively, were added to the gaging water. The mortar specimens were molded at 70° F, placed in a moist closet at 70° F for the first 24 hours, removed and stored in water at the same temperature until tested.

Concrete was tested in the form of 6 by 12-inch cylinders made from a 1:2:4 mix by volume, using local sand and gravel. The amount of water (6.5 gallons per sack) used for gaging gave a cement-water ratio of 1.73 by weight and contained, respectively, 0, 1, 1.5, and 2.25 percent of anhydrous calcium chloride by weight of the cement.

The effect of three curing temperatures on strength was studied by means of plastic mortar tests (10) which were designed to give mortar strengths comparable with those of concrete. Pit-run Ottawa sand was used as the aggregate in the proportion of 1 part of cement to 2.65 parts of sand. The same cement-water ratio and percentages of admixtures of calcium chloride were used as in the concrete tests. The mortar specimens were cured 1 day in the molds at 70, 40, and 90° F. then removed from the molds and stored in water. The curing conditions were:

Storage 1.—Cured at 70° F for 90 days (standard).
Storage 2.—Cured at 40° F for first 28 days, then 70° F.
Storage 3.—Cured at 90° F for first 28 days, then 70° F.

(b) TEST RESULTS

(1). *Time of Set.*—A summary of the setting times for the standard portland cements is shown in figure 6. It will be noted that the average setting time together with, in general, the spread of the time of set, decreases as the amount of calcium chloride is increased. The addition of calcium chloride to the white and high-early-strength

cements, likewise decreases the time of set. All pats, subjected to 5 hours' steaming, both with and without calcium chloride, were sound.

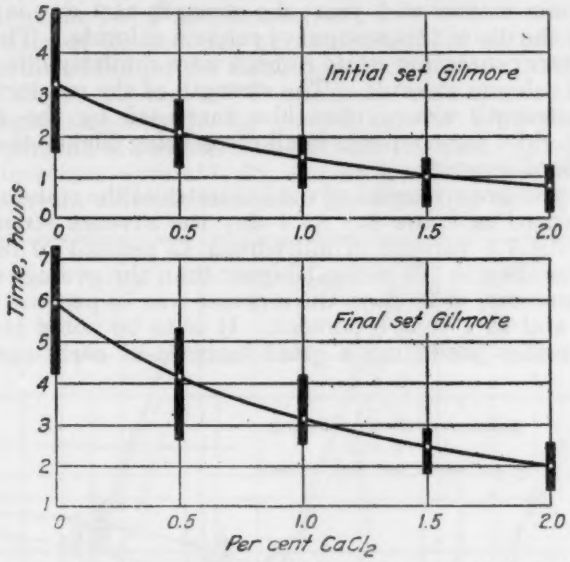


FIGURE 6.—*Setting time of eight standard portland cements.*

(2) *Strengths.*—A summary of the 1:3 standard sand mortar strengths is given in figure 7. This graph shows the strengths of the

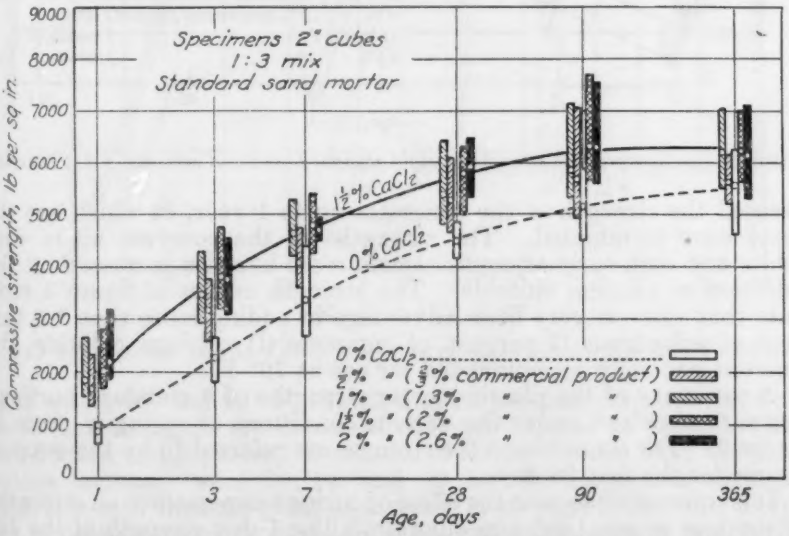


FIGURE 7.—*Compressive strength of eight standard portland cements, 1:3 standard sand mortars.*

standard portland cements with the addition of various percentages of calcium chloride. Not only were the early strengths of portland-cement mortar greatly increased by calcium chloride, but the 1-year

strengths were also increased. The results of the tests show that the mortar containing 1.5 percent of anhydrous (2 percent of commercial) calcium chloride has a strength approximately 15 percent greater than the plain mortar at 1 year; the strength at 1 day is practically doubled by the use of this amount of calcium chloride. The strengths of the mortars containing white cement were similarly affected by the addition of calcium chloride. The strength of the mortar made with high-early-strength cement was also increased by the addition of calcium chloride; the strengths in all cases being higher than those of the 8 standard cements.

The compressive strengths of the concretes of the standard cements are summarized in figure 8. At 1 day the average strength of the concrete with 1.5 percent of anhydrous (2 percent of commercial) calcium chloride was 128 percent higher than the average strength of the plain concrete, at 28 days the increase was 13 percent, at 90 days 9 percent, and at 1 year 8 percent. It is to be noted that calcium chloride, besides producing a great increase at early ages, also in-

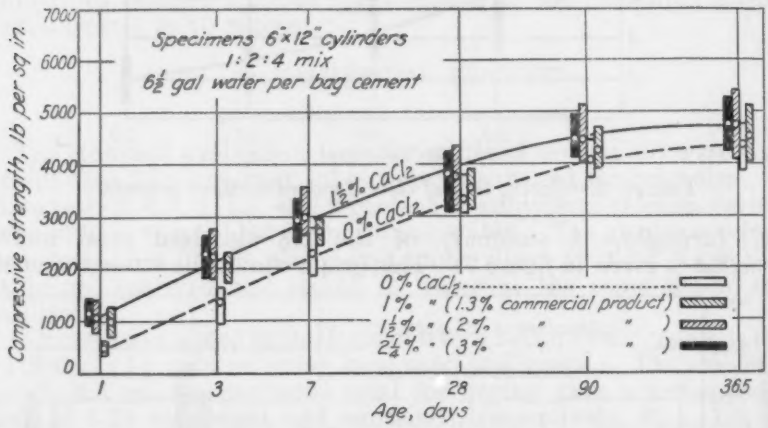


FIGURE 8.—*Compressive strength of eight standard portland cements, 1:2:4 concrete.*

creased the strength of the concretes up to 1 year, at which age the tests were terminated. The strengths of the concrete made with white and high-early-strength cement were likewise increased by the addition of calcium chloride. The strength curves of figure 8 indicate that there is very little advantage in adding more than 1.5 percent of anhydrous (2 percent of commercial) calcium chloride, the amount generally recommended for use at 70° F.

A summary of the plastic mortar strengths of 8 standard portland cements obtained under the various conditions of curing is given in figure 9. For convenience the storages are referred to by the temperatures for the first 28 days.

It is interesting to note the effect of curing temperatures on strengths of mortars without calcium chloride. The 1-day strength of the 40° F specimens is 475 lb/in.^{2} (91 percent) less than that of the 70° F specimens, and the 40° F specimens require approximately 3 days to reach the 1-day strength of the 70° F specimens. At 28 days the 40° F specimens are approximately 1,000 lb/in.^{2} (23 percent) lower

than the 70 ° F specimens. An increase in the storage temperature of 20 degrees, from 70 to 90° F, about doubles the 1-day strength. At both 28 and 90 days the strength of the 90° F specimens is less than the strength of the 70° F specimens.

The strengths of the mortars were increased for all percentages of calcium chloride added for the three storage conditions. At 1 day the strengths of the 40, 70, and 90° F specimens were increased 300, 145, and 90 percent, respectively, by the addition of 1.5 percent of anhydrous (2 percent of commercial) calcium chloride. At 3 days the percentage increases were 117, 68, and 41 for the respective curings. At 7 days calcium chloride increased the strengths of the specimens

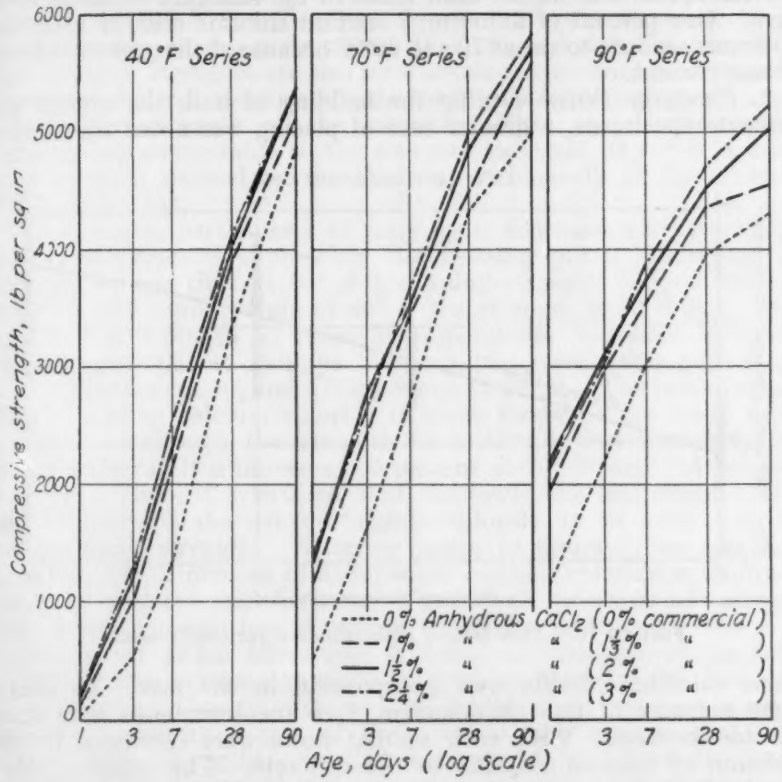


FIGURE 9.—*Average plastic mortar strengths of eight standard portland cements.*

cured at 40, 70, and 90° F, 75, 32, and 23 percent, respectively, but the 28-day strengths are increased only 20, 12, and 15 percent with the addition of 1.5 percent of calcium chloride. At 90 days the percentage increases were 10, 14, and 16 for the respective curings. Thus, it is seen that the greatest increase in strength due to the addition of calcium chloride is obtained at low temperatures and early ages.

It is interesting to note in figure 9, that the 1-day strengths of the specimens with no calcium chloride added, cured at 90° F, are approximately the same as those of the 70° F specimens containing 1.5 percent of anhydrous (2 percent of commercial) calcium chloride.

The increase in strength at 1 day, due to increasing the temperature from 70° to 90° F, is approximately the same as that produced at 70° F by the addition of 1.5 percent of calcium chloride. At 40° F the addition of 1.5 percent of calcium chloride produces approximately the same strength in 2 days that mortars without calcium chloride possess at 70° F in 1 day.

The strengths of the mortars containing white cement were within the same range as those containing standard cement, and the strengths were similarly affected by calcium chloride. Likewise, the strengths of the mortars containing high-early-strength cement were increased by the addition of calcium chloride for all storage conditions, but the strengths were higher than those of the standard cements at all ages. One percent of anhydrous calcium chloride seemed to be the optimum amount to use at 70 and 90° F because of the greater activity of this cement.

3. *Plasticity Tests.*—During the molding of both the mortar and concrete specimens, a greater ease of placing was noted when anhydrous calcium chloride was incorporated in the mix. To obtain some measure of this phenomenon, flow measurements were made on the concrete. With each cement flows were increased by the addition of calcium chloride to the concrete. The range of flows obtained on 8 standard cements as well as the average flow are plotted in figure 10 against the amount of calcium chloride added. The flow is expressed as the percentage increase in diameter after dropping the flow table 15 times, a distance of ⅛ inch.

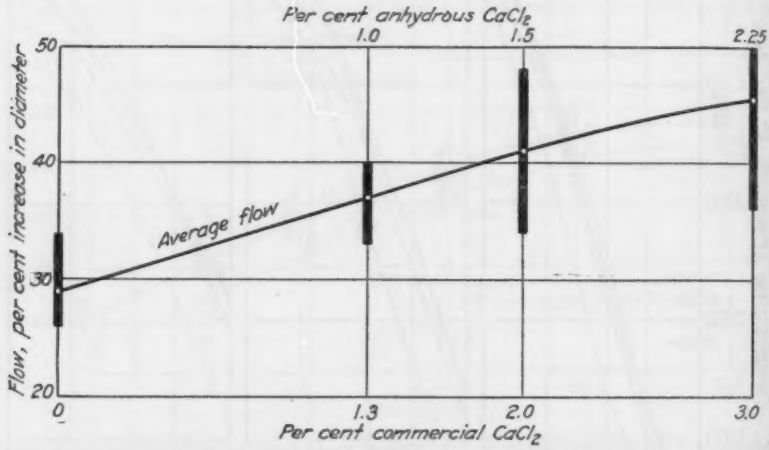


FIGURE 10.—*Flow tests of eight standard portland cements.*

Each point on the average flow curve represents the mean of 72 determinations. There was an increase in the average flow from 29 to 41 with the addition of 1.5 percent of anhydrous calcium chloride.

The flows of the concrete containing white cements were within the same range as the flows with standard cements, and the calcium chloride had approximately the same effect. The flow of the concrete containing high-early-strength cement was similarly increased by the addition of calcium chloride, but the flow was smaller in all

cases, being 16 with 0 percent and 21 with 1.5 percent of calcium chloride.

This increase in flow indicates increased workability. Thus, by adding calcium chloride less water may be used and a flow equal to that of plain concrete may still be obtained. Therefore, not only an increase in strength due directly to the addition of calcium chloride, but also a further increase in strength due to a decreased content of mixing water can be obtained.

V. DISCUSSION AND RECOMMENDATIONS

A comparison of figures 8 and 9 shows that the plastic-mortar strengths at 70° F is sufficiently close to the concrete strengths to be comparable at the early ages. If at 40 and 90° F curing the plastic-mortar strengths are also comparable to the concrete strengths, the data of figure 9 clearly show the marked effect of curing temperature on the strength of the concrete. That the plastic-mortar strengths are comparable to the concrete strengths at 40° F is indicated by data secured by the Highway Laboratory of the District of Columbia (13).

The strength, particularly at early ages, decreases very markedly as the temperature approaches the freezing point. Referring to figure 9, we see that at 90° F the 1-day strength is 1,140 lb/in.^{2}, at 70° F, 520 lb/in.^{2}, while at 40° F the strength is 50 lb/in.^{2} The difference in strength at these 3 temperatures decreased with increasing age until at 28 days the strengths were 4,000 pounds at 90, 4,400 pounds at 70, and 3,300 pounds at 40° F. The proportional effect of adding calcium chloride is much larger at the lower temperatures. Although the strength at 3 days is increased only 28 percent at 90° F, it is increased 60 percent at 70° F, and 115 percent at 40° F. Thus, it is evident that the lower the temperature, the more effective is the use of calcium chloride as an admixture to produce early strength. Referring again to figure 9, we see that up to 90 days, 2 percent of commercial calcium chloride is approximately as effective as 3 percent. There is no economic advantage, then, in using more than 2 percent integrally in the concrete.

There is an added advantage in using calcium chloride in cold weather in the increased rapidity with which it causes the development of heat. Construction at low temperature requires special measures to assure a rate of hydration of the cement that will develop early strengths. In thin concrete slabs, where the heat may be readily dissipated, this increased rapidity of heat development will compensate for some of the heat lost and will decrease the curing time and the time necessary for the use of coverings, or other means of maintaining a satisfactory temperature for hydration (11, 12).

Figure 11 has been prepared to show the length of time that will be required for representative standard and high-early-strength cements, both with and without calcium chloride, at placing and curing temperatures of 40, 70, and 90° F, to obtain a strength of 2,500 lb/in.^{2}. It will be noted from the data (fig. 11) that the amounts of calcium chloride added to the cements at the higher temperatures were less than at the lower temperature. Several factors contributed to the choice of the amounts used.

Lerch and Bogue (3), in a study of the heat of hydration of portland-cement paste, found that higher initial temperatures accelerate the reactions of hydration and increase the quantity of heat liberated from the cements at early ages. Figure 12, which gives a typical graph of the effect of initial temperature on the heat of

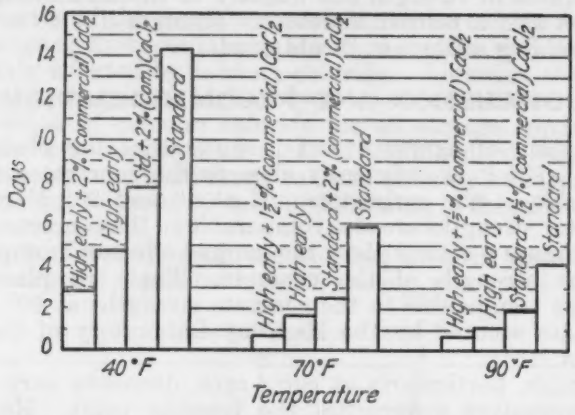


FIGURE 11.—*Effect of curing temperature and addition of calcium chloride on length of time required for concrete to attain 2,500* lb/in.^{2} *strength (based on plastic mortar strength).*

hydration, shows that as the initial temperature is increased the maximum temperature attained is increased, and the time required to reach the maximum temperature is decreased.

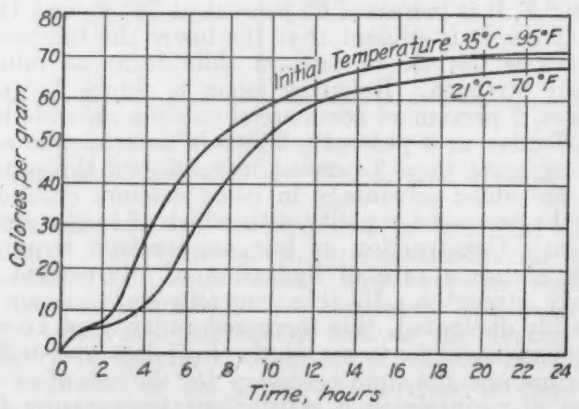


FIGURE 12.—*Typical curves showing the effect of initial temperature on the rate of evolution of heat from portland cement.*

(Reproduced by permission of the Portland Cement Association Fellowship.)

Added to this accelerating effect of the higher temperatures is the accelerating action of calcium chloride which, according to a comparison of heat tests previously mentioned and figure 12, is of equal importance to the acceleration caused by raising the temperature from 70 to 95° F. Therefore, when calcium chloride is

added to cement at a higher temperature, two accelerating actions, which are additive, are superimposed. Several investigators (2, 3, and 14) have shown that there is a direct relation between the rate of evolution of heat, or temperature rise, and the rate of hardening or set. Too great an increase in either, or both, of the accelerating factors, therefore, is likely to cause a time of set so rapid that finishing of the placed concrete would be difficult.

An initial stiffening of the mix occurred at 90° F during the mixing and molding of the plastic-mortar specimens when as much as 3 percent of commercial calcium chloride was added. This made the finishing of some of the specimens difficult. Although with 2 percent of calcium chloride no stiffening was noted, the workability of the mortar, when molded at 90° F, appeared to be at its maximum with only 1.5 percent of commercial calcium chloride present. Mortar with less admixture was less workable.

The recommended amount to be added to the standard and white portland cements at 40 and 70° F was found to be 2 percent of commercial calcium chloride; at 90° F the amount should be decreased to 1.5 percent. Since it has been shown that the accelerating action of both increased initial temperature and calcium chloride is greater for the high-early-strength cement, not more than 1.5 percent of commercial calcium chloride is recommended for high-early-strength cement at either 70 or 90° F (15).

VI. SUMMARY

The following conclusions have been drawn from the investigation:

1. The heat contributed by the 4 major compounds of portland cement during the first 24 hours was determined on neat cement pastes and also with the pastes to which 1 percent of anhydrous calcium chloride was added. Factors are given from which the heat evolved in 24 hours by a portland cement may be computed from its compound composition, either with no calcium chloride or when 1 percent of anhydrous calcium chloride is present. The addition of calcium chloride increased the heat contributed by dicalcium silicate and tetracalcium alumino-ferrite, decreased the heat from tricalcium aluminate, and had little or no effect on the heat contributed by tricalcium silicate.

2. The addition of calcium chloride increased the heat evolved by each of the cements tested up to 24 hours, even though that part of the total heat developed by the tricalcium aluminate was decreased. Although there was not much change in the total heat evolved in 24 hours, the addition of calcium chloride markedly increased the rapidity with which this heat was evolved.

3. Sixty experimental portland cements were grouped according to the amount of heat evolved during the first 24 hours of hydration. It was found that for the group that developed only 30 to 40 calories per gram, the addition of 1 percent of anhydrous calcium chloride increased the heat 7 calories per gram. Groups which evolve greater amounts of heat liberate less and less heat with the addition of calcium chloride, until in that group liberating from 70 to 80 calories per gram the addition of calcium chloride lowers the amount of heat liberated by 2 calories per gram.

4. The study (at 70° F) of the mortar strengths of 60 experimental portland cements of widely varying composition at ages up to 28 days, beyond which no measurements were made, shows:

(a) Corroborating the findings of other investigators, the compound composition of portland cement greatly influences its strength. The strength contributed by each of the four major components has been computed.

(b) Calcium chloride increased the strengths of cement mortars, especially marked when the composition of the cement was within the range encountered in commercial portland cements.

(c) The addition of calcium chloride increased the strength contributed by dicalcium and tricalcium silicates.

(d) The addition of calcium chloride increased the strength contributed by tricalcium aluminate for the first few days, but after this time decreased the strength contributed by this compound.

(e) The contribution of tetracalcium alumino-ferrite to the strength is small. The addition of calcium chloride appears to make this factor slightly negative at all ages.

5. The tests of 8 standard, 2 white and 1 high-early-strength commercial portland cements, selected to obtain large variations in composition, show:

(a) The setting times of cement at 70° F were decreased by the addition of increasing amounts of calcium chloride.

(b) The addition of calcium chloride increased the strength of each of the cements at all ages up to 1 year, beyond which tests were not made. Not only were the early strengths greatly increased by the addition of calcium chloride, but the 1-year strengths were appreciably increased. Tests at 40 and 90° F also showed an increased strength at all ages up to 90 days, at which time the tests were terminated.

(c) At 70° F the flow or workability of the concrete was increased by the addition of calcium chloride up to and including 3 percent of commercial calcium chloride.

(d) Tests at 40, 70, and 90° F showed that the lower the initial curing temperatures the more effective is the use of calcium chloride as an admixture in increasing the early strength.

(e) Integral use of calcium chloride was effective in accelerating the curing of all the cements. It is, therefore, of value in cold-weather construction in decreasing the time necessary for protecting the concrete.

6. A tabulation is given showing the time required for normal portland and high-early-strength portland cements to attain a compressive strength of 2,500 lb/in.^{2} The effects of different curing temperatures, both with and without calcium chloride, are given. The optimum amount of calcium chloride which should be used at the three curing temperatures studied, was found to be:

Temperatures	Commercial calcium chloride	Type of cement
°F	*Percent*	
40	2	All cements.
70	2	Normal and white.
	1.5	High early.
90	1.5	All cements.

In carrying out the work in connection with this paper the author wishes to thank C. A. Hogentogler, Jr., for his help in preparing many of the test specimens, W. D. Foster in calculating many of the heat data, and P. W. Downey for his assistance in preparing the report. Thanks are also expressed to P. H. Bates, L. S. Wells, and H. F. Clemmer for their assistance in the progress of this research.

VII. REFERENCES

(1) Proc.Highway Research Board **13,** 291 (Dec. 1933).
(2) Proc.Am.Concrete Inst. **26,** 65 (1930).
(3) J.Research NBS **12,** 645 (1934) RP684.
(4) Ind.Eng.Chem. **1,** (Anal. ed.) 192 (1929).
(5) Proc.Am.Concrete Inst. **30,** 9 (1934).
(6) Ind.Eng.Chem. **24,** 1207 (1932).
(7) Proc.Am.Soc.Testing Materials **34,** (part II) 244 (1934).
(8) Eng.News-Record **107,** 130 (1931).
(9) Federal Specification SS–C–91 for Cement, Portland, Am.Soc.Testing Materials Serial Designation C77–32.
(10) Proc.Am.Soc.Testing Materials **28,** (part II) 43 (1928).
(11) Proc.Am.Soc.Testing Materials **31,** (part I) 347 (1931).
(12) Proc.Highway Research Board **9,** (part I) 369 (Dec. 1929).
(13) Am.Road Builders Assn.Bul. 42 (1934).
(14) Chimieet industrie **31,** 1291 (1934).
(15) Am.Soc.Testing Materials Designation C82–34.

WASHINGTON, January 29, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP783

Part of Journal of Research of the National Bureau of Standards, Volume 14, April 1935

ARC SPECTRUM OF COPPER IN THE INFRARED

By C. C. Kiess

ABSTRACT

A survey of the arc spectrum of copper out to the limit attainable photographically in the infrared has yielded about 30 new lines. All, except one, are accounted for as combinations between previously known terms of Cu I.

INTRODUCTION

The new types of photographic plates that the Eastman Kodak Co.[1] has introduced, in recent years, have made it possible to record infrared spectra out to 12000 A, and even somewhat beyond. These plates have been extensively used in the spectroscopy laboratory of the National Bureau of Standards to make systematic surveys of the near infrared spectra of most of the chemical elements. For some of the elements, results have already been published in several papers,[2] to which reference should be made for a description of the apparatus and methods employed in these investigations. It is the purpose of this paper to present the infrared wave lengths that have been measured in the arc spectrum of copper.

The radiometric survey of the infrared arc spectrum of copper, made in 1910 by Randall,[3] revealed only six lines between 7000 and 30000 A. Two of these form the intense doublet at 7933 and 8092 A which, subsequently, have had their wave lengths accurately determined from photographic observations.[4] The other four lines lie between 16000 and 18000 A, and are still beyond the reach of photographic methods. The lines longer than 8100 A observed in the copper arc by Meggers, are, with one exception, mostly attributable to the atmospheric gases, nitrogen and oxygen, which are excited when an electric arc passes between metallic electrodes in air.

The existence of lines in the infrared arc spectrum of copper may be predicted from the terms of Cu I given by Shenstone,[5] who has made a practically complete analysis of the spectrum. In this analysis it is shown that nearly all the observed lines are accounted for as combinations between the doublet and quartet terms required by atomic theory. These terms arise from the addition of $s,p,d,\cdots$, electrons to the electron configurations d^{10} and d^9s, which characterize the low and

[1] Mees, J.Opt.Soc.Am. **22**, 204 (1932).
[2] BS Research Papers RP473, RP558, and RP624.
[3] Randall, Astrophys. J. **34** 8 (1911).
[4] Eder, Sitz.Ber.Akad.Wiss.Wien IIa **124**, 110 (1915). Meggers, BS Sci.Pap. **14**, 385 (1918). Burns and Walters, Pub. Allegheny Observatory **8**, 34 (1930).
[5] Phys. Rev. **28**, 449 (1926).

metastable energy states of the singly ionized atom. It is of interest to note that most of the intense, sharp lines of the copper arc involve the doublet terms of the d^{10} configuration, whereas all but a few of the numerous hazy and diffuse lines involve the doublet and quartet terms of the d^9s configuration.

TABLE 1.—*New lines in arc spectrum of* Cu

λ_{air}A	Intensity and notes	Wave number (vac.)	Term combination
11118. 2	1*h*	8991. 8	$m4p\ {}^4P^0_{3/2}$—$k4d\ {}^2D_{1\frac{1}{2}}$
10883. 3	1	9185. 8	$k5p\ {}^2P^0_{1/2}$—$k8s\ {}^2S_{0\frac{1}{2}}$
10771. 7	2*H*	9281. 0	$n4p\ {}^2D^0_{1\frac{1}{2}}$—$n5s\ {}^2D_{1\frac{1}{2}}$
10179. 2	1	9821. 2	$m4p\ {}^4P^0_{1/2}$—$k4d\ {}^2D_{1\frac{1}{2}}$
10172. 00	20	9828. 23	$m4p\ {}^4P^0_{1/2}$—$k4d\ {}^2D_{2\frac{1}{2}}$
10146. 78	50*b*	9852. 64	$n4p\ {}^2F^0_{2\frac{1}{2}}$—$n5s\ {}^2D_{1\frac{1}{2}}$
10124. 5	5*H*	9874. 3	$k6p\ {}^2P^0_{1/2}$—$m5s\ {}^2D_{2\frac{1}{2}}$
9739. 6	4*H*	10264. 6	$k5p\ {}^2P^0_{1/2}$—$k9s\ {}^2S_{0\frac{1}{2}}$
9688. 5	2*H*	10318. 7	
9530. 3	10*H*	10490. 0	$n4p\ {}^2D^0_{2\frac{1}{2}}$—$n5s\ {}^2D_{2\frac{1}{2}}$
9472. 4	2*H*	10554. 1	$k7p\ {}^2P^0_{2\frac{1}{2}}$—$n5s\ {}^2D_{1\frac{1}{2}}$
9263. 0[a]	2*b*	10792. 7	$m4p\ {}^2P^0_{1/2}$—$k7s\ {}^2S_{0\frac{1}{2}}$
9256. 8	1*H*	10799. 9	$n4p\ {}^2P^0_{1/2}$—$n5s\ {}^2D_{2\frac{1}{2}}$
9213. 5	2*H*	10850. 7	$m4p\ {}^2P^0_{3/2}$—$k7s\ {}^2S_{0\frac{1}{2}}$
8996. 2	8*H*	11112. 7	$n4p\ {}^2F^0_{3/2}$—$n5s\ {}^2D_{2\frac{1}{2}}$
8831. 3	1*b*	11320. 3	$n4p\ {}^2D^0_{2\frac{1}{2}}$—$n5s\ {}^2D_{1\frac{1}{2}}$
8584. 0	5*b*	11646. 4	$k5s\ {}^2S_{0\frac{1}{2}}$—$k6p\ {}^2P^0_{1/2}$
8408. 15	10*b*	11889. 96	$k5s\ {}^2S_{0\frac{1}{2}}$—$k6p\ {}^2P^0_{3/2}$
8006. 21	4	12486. 87	$n4p\ {}^2D^0_{1\frac{1}{2}}$—$m4d\ {}^4P_{2\frac{1}{2}}$
7000. 0	1*h*	14281. 8	$k5s\ {}^2S_{0\frac{1}{2}}$—$k7p\ {}^2P^0_{3/2}$
6968. 34	1*b*	14346. 67	$n4p\ {}^2D^0_{2\frac{1}{2}}$—$m4d\ {}^4S_{1\frac{1}{2}}$
6634. 7	1*h*	15068. 0	$n4p\ {}^2F^0_{3/2}$—$m4d\ {}^2D_{2\frac{1}{2}}$
6433. 35	1	15539. 72	$n4p\ {}^2P^0_{1/2}$—$m4d\ {}^4P_{0\frac{1}{2}}$
6373. 3	1	15686. 1	$k7p\ {}^2P^0_{3/2}$—$m4d\ {}^2S_{0\frac{1}{2}}$
6165. 7	1*h*	16214. 3	$k6p\ {}^2P^0_{1/2}$—$m4d\ {}^4S_{1\frac{1}{2}}$
5727. 9	2*h*, *l*	17453. 6	$n4p\ {}^2F^0_{2\frac{1}{2}}$—$n4d\ {}^2F_{3\frac{1}{2}}$
5646. 6	1*h*	17704. 9	$m4p\ {}^2P^0_{1/2}$—$m5s\ {}^4D_{1\frac{1}{2}}$
5629. 2	1*H*	17759. 6	$k5p\ {}^2P^0_{1/2}$—$n5s\ {}^2D_{2\frac{1}{2}}$

[a] Blended with 9262.8 of oxygen.

Note. k=$3d^{10}$ (^{1}S); m=$3d^94s$ (^{3}D); n=$3d^94s$ (^{1}D).

RESULTS

The new wave lengths for copper are given in table 1 and represent the average of two to eight observations, except for a few lines, observed on only one plate. The spectrograms, from which they were derived, were taken according to the experimental procedure described in the papers cited above, and required exposures of 2 and 3 hours. Most of the lines are diffuse and very hazy, which is indicated by the symbols *h* and *H* following the intensity estimate. A few of the lines appear to be widened, without, however, showing the haziness presented by the others. This characteristic is denoted by *b*. The letter *l* indicates an unsymmetrical shading of the line toward longer wave lengths.

All but one of the new lines are accounted for as combinations between the terms given by Shenstone. These terms, however, are not designated by the symbols originally assigned by him, but by those conforming to present usage, given by Bacher and Goudsmit.[6] It is of interest to note that nearly all the new hazy lines also involve terms belonging to configurations containing the d^9s electrons.

In addition to the new infrared lines, table 1 also contains some lines of Cu I which have been measured at various times at the National Bureau of Standards, during the spectroscopic examination of materials for which copper rods were used as supporting electrodes. These lines, which do not appear in any of the published lists of wave lengths are all satisfactorily accounted for by Shenstone's terms, and are, therefore, presented at this time to extend the description of Cu I.

WASHINGTON, January 23, 1935.

[6] Bacher and Goudsmit, Atomic Energy States, page 175 (McGraw-Hill Book Co., New York, 1932).